NOTIZEN

Magnetic Susceptibility and Structure of Some Transition Metal(II) Complexes with 1,2,4-Triazole

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The magnetic susceptibilities of some transition metal(II) complexes with 1,2,4-triazole (trz) have been measured in the range 2 – 300 K.

$Ni(trz)_2(NO_3)_2(H_2O)_{8/3}$, $Ni(trz)_2SO_4(H_2O)_5$ and α-$Ni(trz)_2(NCS)_2$

are found to be linear antiferromagnetic trimers. For β-$Ni(trz)_2(NCS)_2$ and similar compounds with Mn(II), Fe(II), Co(II) and Cu(II), totally different magnetic properties were observed, suggesting the presence of two-dimensional networks of metal ions bridged by 1,2,4-triazole molecules. For $Co(trz)_2(NCS)_2$ this was confirmed by X-ray single crystal diffraction.

The magnetic susceptibilities of powdered $Ni(trz)_2(NO_3)_2(H_2O)_{8/3}$ [1], $Ni(trz)_2SO_4(H_2O)_5$ and α-$Ni(trz)_2(NCS)_2$ [2] have been measured in the range 2 – 300 K. The nitrate complex was shown by Reimann and Zocchi [1] to consist of isolated linear trimers, with nickel ions bridged by triazole molecules. A close resemblance was found between the infra-red spectra of the three complexes. From the ligand field spectra the nickel ions appear to be octahedrally coordinated [2].

The magnetic behaviour of the nitrate complex is that expected for a linear trimer having antiferromagnetic intramolecular exchange [3].

The sulphate and thiocyanate show a similar magnetic behaviour, thus ruling out the possibilities of dimers, tetramers or linear chains.

With exchange between adjacent nickel ions only, a reasonable fit was obtained using Ginsberg's formula [3]. The exchange parameters of the three complexes did not differ significantly, values of -12.5 ± 0.5 K were found, with $g = 2.13 \pm 0.03$.

The magnetic properties of powdered samples of β-$Ni(trz)_2(NCS)_2$ [2] and its related compounds with Mn(II), Fe(II), Co(II) and Cu(II) appear to be surprisingly different from what may be expected for cluster-like coordination compounds [4].

The susceptibilities as a function of temperature of the Co(II) and Fe(II) complexes, measured at fields of about 0.5 kOe and 1.5 kOe respectively are alike, showing very sharp maxima at 5.9 K and 8.8 K, respectively. The magnetization curves at 2.2 K of the Co(II) and Fe(II) complexes are also similar. With increasing field strength a sharp increase of the magnetization is observed (approximately 15 times) at about 1.0 kOe and 1.7 kOe respectively. After the S-shaped jump the slope of the curve increases gradually up to 56 kOe. Furthermore, with decreasing field strength the compounds show a considerable hysteresis with a zero field residual moment of about 0.05 B.M. The susceptibility of the Mn(II) complex shows a broader peak at 3.9 K. In the magnetization curve a spin-flop transition occurs at about 11 kOe. The maximum in the susceptibility vs. temperature curve of the β-Ni(II) complex is again broader. The magnetization curve, measured at 4.2 K starts at a zero field moment of 0.011 B.M. It then increases linearly to 10 kOe, where the slope increases and a straight line is followed up to 56 kOe. For the Cu(II) complex susceptibility measurements down to the lowest temperature of 2 K that can be obtained with our equipment (a PAR vibrating sample magnetometer model 150A with Janis cryostat) only permitted to see the onset of magnetic ordering, if any.

From the following observations a possible structure for these complexes may be predicted:

1. The magnetic data show clearly that the complexes are of a polynuclear nature.
2. The infrared spectra indicate the triazole molecules to act as bidentate 2,4 coordinating ligands.
3. The NCS groups are N-donors [2], thus completing the $M(II)N_6$ octahedra.

The available data may be explained by assuming the presence of two-dimensional M(II) networks with 2,4 bridging triazole molecules and the NCS groups on either side of the planes. The observation of a zero field residual moment suggests the $M(II)N_6$ octahedra to be tilted.

This model has been confirmed by X-ray diffraction experiments on a $Co(trz)_2(NCS)_2$ single crystal [5]. The compound is orthorhombic, space group Aba2, with $a = 7{,}800$ Å, $b = 16{,}333$ Å, $c = 9{,}740$ Å and $Z = 4$. The Co(II) ions occupy special positions $(0, 0, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$. The two-dimensional Co(II) layers are thus lying in the 010 and 020 planes. The bridging triazole molecules are almost parallel to the

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b-axis. The Co(II)N_6 octahedra are tilted in the *a*-*b* plane with respect to the *b* axis at an angle of 31°.

Apart from a more detailed study of the magnetic behaviour of the powdered samples, single crystal magnetic measurements, neutron diffraction experiments, E.S.R. and heat capacity measurements will be performed [4].

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