Magnetic and Spectroscopic Properties of Metal(II) Thiocyanate Compounds with 3,4-Dialkyl Substituted 1,2,4-Triazoles

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Z. Naturforsch. 42b, 791—795 (1987); received January 19, 1987

Asymmetric 1,2,4-Triazoles, Magnetic Exchange, Binuclear Compounds, Thiocyanate

Syntheses, spectroscopic and magnetic properties are described of a series of metal(II) thiocyanate compounds with the asymmetric ligands 3-methyl-4-ethyl-1,2,4-triazole and 3-methyl-4-tert-butyl-1,2,4-triazole. A dinuclear structure is proposed for the manganese, cobalt and nickel compounds based on the magnetic behaviour as well as on spectroscopic and analytical data. These compounds show antiferromagnetic interaction in the temperature range 4—80 K. The zinc compounds appear to be mononuclear, whereas a chain-like structure is proposed for the cadmium compounds.

Introduction

Recently we reported the results of the investigations on 3,4-disubstituted 1,2,4-triazole ligands [1]. Metal(II) trifluoromethanesulfonates have been synthesized with 3-methyl-4-ethyl-1,2,4-triazole (abbr. as metz) and 3-methyl-4-tert-butyl-1,2,4-triazole (abbr. as mtbtz) as ligands. In most cases linear trinuclear compounds have been obtained in which the metal centers are linked to each other through triple triazole bridges. The structure of [Co₄(metz)₃(H₂O)₆][Co₄(metz)₃(H₂O)₆](CF₃SO₃)₁₂(H₂O)₁₀ has been elucidated [1]. These investigations are a propagation of the research on 4-alkyl substituted triazoles, carried out during the last decade [2—10]. Attention is given to the magnetic properties of the coordination compounds in relation to their structural parameters.

In addition to non-coordinating CF₃SO₃⁻, the thiocyanate anion which coordinates easily to metal ions through its N-atom, was used to synthesize coordination compounds with this new type of asymmetric triazole ligands. The results of these investigations are described below.

Experimental Section

Syntheses

The ligands metz and mtbtz have been prepared from acetylhydrazine, triethylorthoformate and ethylamine or tert-butyamine, respectively, as described elsewhere [1, 11].

All coordination compounds crystallized within two days upon standing at room temperature. The crystals were filtrated, washed with a small amount of ethanol and dried on air.

Synthesis of [Mn₃(NCS)₄(metz)₂(H₂O)]: A solution of 2 mmol of MnCl₂·4H₂O and 4 mmol of NH₄NCS in 5 ml of water was added to a solution of 2 mmol of metz in 5 ml of water.

Synthesis of [M₃(NCS)₄(metz)₂(H₂O)₂ (M = Co, Ni): A solution of 2 mmol of MCl₂·6H₂O and 4 mmol of NH₄NCS in 10 ml of ethanol/water (1:1) was added to a solution of 6 mmol of metz in 10 ml of ethanol/water (1:1).

Syntheses of [Cu₃(NCS)₄(metz)₂] and Zn(NCS)₂(metz)₂: A solution of 2 mmol of CuCl₂·2H₂O and ZnCl₂·2H₂O resp. and 4 mmol of NH₄NCS in 10 ml of water was added to a solution of 6 mmol of metz in 10 ml of water.

Synthesis of [Mn₂(NCS)₄(mtbtz)₂(H₂O)]: A solution of 2 mmol of MnCl₂·4H₂O and 4 mmol of NH₄NCS in 5 ml of water was added to a solution of 6 mmol of mtbtz in 5 ml of water.

Synthesis of [Co₂(NCS)₄(mtbtz)₂(H₂O)]: A solution of 2 mmol of CoCl₂·4H₂O and 4 mmol of NH₄NCS in 10 ml of ethanol/water (1:1) was added to a solution of 6 mmol of mtbtz in 10 ml of ethanol/water (1:1).

Synthesis of [Ni₂(NCS)₄(mtbtz)₂(H₂O)]: A solution of 2 mmol of CoCl₂·4H₂O and 4 mmol of NH₄NCS in 5 ml of ethanol was added to a solution of 6 mmol of mtbtz in 5 ml of ethanol.

Synthesis of Zn(NCS)₂(mtbtz)₂: A solution of 2 mmol of ZnCl₂·4H₂O and 4 mmol of NH₄NCS in 10 ml of ethanol/water (1:1) was added to a solution of 4 mmol of mtbtz in 10 ml of ethanol/water (1:1).

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Synthesis of \([\text{Cd}(\text{NCS})_2(\text{metz})]_2\): A solution of 2 mmol of \(\text{CdCl}_2\cdot 4\text{H}_2\text{O}\) and 4 mmol of \(\text{NH}_2\text{NCS}\) in 10 ml of ethanol was added to a solution of 6 mmol of metz in 10 ml of ethanol.

Synthesis of \([\text{Cd}(\text{NCS})_2(\text{mtbtz})]_2\): A solution of 2 mmol of \(\text{CdCl}_2\cdot 4\text{H}_2\text{O}\) and 4 mmol of \(\text{NH}_2\text{NCS}\) in 10 ml of ethanol was added to a solution of 4 mmol of mtbtz in 10 ml of ethanol.

Analyses and spectroscopic measurements

C, H, and N determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland. Metal analyses have been done inhouse, using standard EDTA titrations.

Infrared spectra have been recorded as KBr pellets in the range 4000—180 cm\(^{-1}\) on a Perkin Elmer 580 spectrofotometer equipped with a Perkin Elmer datastation. UV/Visible spectra were obtained on a Perkin Elmer 330 spectrofotometer using the diffuse reflectance technique, with MgO as a reference.

A PAR vibrating sample magnetometer model 150 A has been used to measure magnetic susceptibilities in the temperature range 4—80 K. Fitting magnetic data to the proper theoretical expressions (vide infra) was performed on a Commodore PC 10 personal computer by means of a Simplex routine [12]. The used program was written by R. Prins.

All parameters \((J, J', g, D \text{ (vide infra)})\) were independently variable in the fitting procedure. The applied expressions for the magnetic susceptibilities were based on the spin Hamiltonian of the form: \(\mathbf{H} = -2\Sigma_{ij} S_i S_j\).

### Results and Discussion

#### General

The compounds obtained with both ligands metz and mtbtz have been tabulated in Table I, together with their analytical and spectroscopic data.

The infrared absorptions of the thiocyanate anion are a strong tool in determining the coordination behaviour of the anion in the compounds under study [15, 16]. The compounds listed in Table I except for the cadmium compounds, all exhibit almost the same values for the \(\nu_{\text{CS}}\) and the \(\nu_{\text{CS}}\) vibrations, i.e. 2070 cm\(^{-1}\) and 790 cm\(^{-1}\) respectively. The \(\nu_{\text{CS}}\) absorptions in the metz compounds, except for \(\text{Zn}(\text{NCS})_2(\text{metz})_2\) and \([\text{Cd}(\text{NCS})_2(\text{metz})]_2\), are observed as a shoulder on an unassigned ligand vibration and therefore the band positions cannot be determined accurately. However, the positions of \(\nu_{\text{CN}}\) and \(\nu_{\text{CS}}\) clearly indicate N-coordinating thiocyanate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental analysis [%]*</th>
<th>X-ray type</th>
<th>Ligand field bonds ([10^3 \text{ cm}^{-1}])</th>
<th>Dq&lt;sup&gt;b&lt;/sup&gt;</th>
<th>B&lt;sup&gt;b&lt;/sup&gt;</th>
<th>m.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mn}(\text{metz})_2(\text{NCS})_4])</td>
<td>white</td>
<td>12.04 38.06 5.24 29.59</td>
<td>A</td>
<td>- - -</td>
<td>- -</td>
<td>&gt;196</td>
<td></td>
</tr>
<tr>
<td>([\text{Co}(\text{metz})_2(\text{NCS})_4])</td>
<td>red</td>
<td>12.01 38.04 5.14 29.07</td>
<td>B</td>
<td>9.54 15.8 20.2</td>
<td>1040 790</td>
<td>125 d&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>([\text{Ni}(\text{metz})_2(\text{NCS})_4])</td>
<td>purple</td>
<td>12.53 36.99 5.21 28.27</td>
<td>B</td>
<td>10.7 17.6 27.6</td>
<td>1020 875</td>
<td>&gt;200</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}(\text{NCS})_2])</td>
<td>green</td>
<td>12.55 37.27 5.20 28.64</td>
<td>C</td>
<td>14.5</td>
<td></td>
<td>140 d</td>
<td></td>
</tr>
<tr>
<td>([\text{Zn}(\text{metz})_2(\text{NCS})_4])</td>
<td>white</td>
<td>12.49 37.00 5.21 28.29</td>
<td>C</td>
<td>14.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Cd}(\text{NCS})_2(\text{metz})_2])</td>
<td>white</td>
<td>13.82 36.06 4.07 28.22</td>
<td>D</td>
<td>7.23 16.7&lt;sup&gt;e&lt;/sup&gt;</td>
<td>- -</td>
<td>&gt;250</td>
<td></td>
</tr>
<tr>
<td>([\text{Cd}(\text{NCS})_2(\text{mtbtz})_2])</td>
<td>white</td>
<td>16.21 35.70 4.46 27.77</td>
<td>E</td>
<td>- - -</td>
<td>- -</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>([\text{Zn}(\text{mtbtz})_2(\text{NCS})_4])</td>
<td>white</td>
<td>30.24 27.17 3.07 22.06</td>
<td>E</td>
<td>- - -</td>
<td>- -</td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>([\text{Co}(\text{mtbtz})_2(\text{NCS})_4])</td>
<td>white</td>
<td>30.62 26.96 3.06 21.93</td>
<td>F</td>
<td>- - -</td>
<td>- -</td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>([\text{Zn}(\text{mtbtz})_2(\text{NCS})_4])</td>
<td>white</td>
<td>10.40 43.45 6.41 25.22</td>
<td>G</td>
<td>9.47 16.4</td>
<td>20.2</td>
<td>1035 790</td>
<td>145</td>
</tr>
<tr>
<td>([\text{Cd}(\text{NCS})_2(\text{mtbtz})_2])</td>
<td>white</td>
<td>10.86 42.83 6.25 24.77</td>
<td>G</td>
<td>10.7 17.5</td>
<td>27.6</td>
<td>1065 870</td>
<td>&gt;240</td>
</tr>
<tr>
<td>([\text{Zn}(\text{mtbtz})_2(\text{NCS})_4])</td>
<td>white</td>
<td>10.86 43.31 6.39 24.62</td>
<td>G</td>
<td>10.7 17.5</td>
<td>27.6</td>
<td>1065 870</td>
<td>&gt;240</td>
</tr>
<tr>
<td>([\text{Cd}(\text{NCS})_2(\text{mtbtz})_2])</td>
<td>white</td>
<td>11.06 42.20 6.14 24.70</td>
<td>G</td>
<td>10.7 17.5</td>
<td>27.6</td>
<td>1065 870</td>
<td>&gt;240</td>
</tr>
<tr>
<td>([\text{Zn}(\text{mtbtz})_2(\text{NCS})_4])</td>
<td>white</td>
<td>14.38 41.44 5.68 24.51</td>
<td>H</td>
<td>- - -</td>
<td>- -</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>([\text{Cd}(\text{NCS})_2(\text{mtbtz})_2])</td>
<td>white</td>
<td>14.23 41.80 5.66 24.38</td>
<td>I</td>
<td>11.0 20.2</td>
<td>27.2&lt;sup&gt;e&lt;/sup&gt;</td>
<td>- -</td>
<td>220</td>
</tr>
</tbody>
</table>

* The second lines give calculated values; b Dq and B values are calculated as in refs [13] and [14]; c d means decomposition; d sulfur analysis: found: 15.62; calcd: 15.87%; e cobalt(II) dope; f copper(II) dope.
As has been explained in a previous paper concerning these ligands [1], no information about the coordination mode of the ligand can be obtained from the IR spectra due to the asymmetry of the ligands. Hereafter some comments will be given on the reported compounds.

\[ \text{[M}_2(NCS)_4(L)_5(H_2O)_X} \] 
(M = Mn, x = 1; M = Co, Ni, x = 2) (L = metz, mtbtz)

The magnetic susceptibility curves of these compounds strongly indicate dinuclear structures. The X vs. T-curves exhibit maxima at 2, 11 and 33 K for M = Mn, Co and Ni respectively. Satisfactory fittings to theoretical expressions [17—19] could also be performed, which confirms the dinuclear character of the compounds. The magnetic parameters, that have been obtained, are tabulated in Table II. The observed and calculated \( g \) vs. T curves for \[ \text{[Ni}_2(NCS)_4(metz)_3(H_2O)_2} \] are given in Fig. 1 as a typical example. The \( g \) values as given in Table II are averaged \( g \) values for the two different metal sites present in the compound. From powder susceptibilities recorded now no information can be obtained about the local \( g \) tensors. Fitting the magnetic data of the two manganese compounds yielded rather low \( g \) values (see Table II). This might be due to a zero field splitting, which could be observed in the ESR spectra, but which was not taken into account in the fitting procedure. The high \( g \) value for \[ \text{[Co}_2(mtbz)_3(NCS)_4(H_2O)} \] might indicate that this compound is not a pure Ising system.

Engelfriet et al. [20, 21] have reported dinuclear compounds with the same composition using the ligands 4-phenyl-1,2,4-triazole and 4-methyl-1,2,4-triazole. It seems likely, that the now described compounds have the same overall structure, i.e. two metal ions bridged by three bidentate triazole ligands, one monodentate ligand at each metal ion and two N-donating NCS~ groups at both cations completing the MN\(_6\) octahedra. A schematic drawing of the structure of these compounds is given in Fig. 2.

Due to the presence of a substituent on C3, the dinuclear compounds must be asymmetric, i.e. all three substituents are pointing to the same side of the cluster or one methyl group is positioned opposite to the other two. The highest grade of asymmetry would have been reached in the case that, due to steric hindrance from the methyl groups, the monodentate coordinating ligands were connected to the same metal ion. The asymmetry of the complex will effect the IR absorptions of the compounds, e.g. nonequivalent thiocyanate groups will give rise to a splitting or broadening of \( \nu_{CN} \). However, such broadenings, which have in fact been observed, could also be ascribed to possible disorder in the...

### Table II. Magnetic data of dinuclear metal(II) thiocyanate compounds with metz and mtbtz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>J [cm(^{-1})]</th>
<th>g</th>
<th>zJ' [cm(^{-1})]</th>
<th>D* [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{Mn}_2(metz)_3(NCS)_4(H_2O)_2 ]</td>
<td>0.4</td>
<td>1.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[ \text{Co}_2(metz)_3(NCS)_4(H_2O)_2 ]</td>
<td>9.9</td>
<td>5.19 (Ising)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[ \text{Ni}_2(metz)_3(NCS)_4(H_2O)_2 ]</td>
<td>11.2</td>
<td>2.32</td>
<td>-1.7</td>
<td>-1.3</td>
</tr>
<tr>
<td>[ \text{Cu}_2(metz)_3(NCS)_4 ]</td>
<td>8.8</td>
<td>2.10</td>
<td>0.02**</td>
<td></td>
</tr>
<tr>
<td>[ \text{Mn}_2(mtbz)_3(NCS)_4(H_2O)_2 ]</td>
<td>0.3</td>
<td>1.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[ \text{Co}_2(mtbz)_3(NCS)_4(H_2O)_2 ]</td>
<td>10.6</td>
<td>8.88 (Ising)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[ \text{Ni}_2(mtbz)_3(NCS)_4(H_2O)_2 ]</td>
<td>9.9</td>
<td>2.12</td>
<td>-1.8</td>
<td>-1.3</td>
</tr>
</tbody>
</table>

* J is intracluster exchange integral; zJ' is intercluster exchange integral; D is zero field splitting parameter; ** percentage of paramagnetic impurity.

![Fig. 1. Susceptibility vs. temperature curves for \[ \text{[Ni}_2(metz)_3(NCS)_4(H_2O)_2} \]. Full curve has been calculated as has been explained in the text. The other compounds reported here show similar susceptibility curves.](image1)

![Fig. 2. Schematic drawing of the structure of \[ \text{[M}_2(L)_3(NCS)_4(H_2O)} \]. M = Mn (x = 1), Co, Ni (x = 2). The indicated positions of the C3 methyl substituents are arbitrary, and cannot be obtained from the spectral data.](image2)
sulfur atoms of the thiocyanate anions [22]. It appeared to be impossible to derive conclusions about the position of the substituents and/or the monodentate ligands from the IR spectra.

\[ \text{Cu}_2(\text{NCS})_4(\text{metz})_3 \]

As for the compounds discussed above, the magnetic susceptibility vs. temperature curve clearly indicates a dinuclear structure for [Cu_2(\text{NCS})_4(\text{metz})_3]. Fitting to the well-known Bleaney-Bowers equation [23] resulted in \( g = 2.10, \ J = -8.8 \text{ cm}^{-1} \) with 2% of a paramagnetic impurity [24]. The EPR spectrum at 77 K strongly confirms the dinuclear nature of the compound. It shows a typical triplet spectrum with a \( \Delta m_s = 2 \) absorption at \( g = 4.3 \) and absorptions at \( g < 2. \) Applying the formalism given by Reedijk [25], the following parameters have been calculated: \( g_s = 2.08(8), \ g_u = 2.10(7), \ g_c = 2.18(7), \ D = 0.08(1) \) and \( E = 0.008(1) \text{ cm}^{-1} \).

For this compound a structure is proposed in which again three bridging triazoles occur between two copper ions, on each copper ion two thiocyanate anions are coordinated. Since no other donating atoms are present the copper atoms are pentacoordinated which is in agreement with the ligand field maximum at 14,500 cm\(^{-1}\).

\[ \text{Zn(\text{NCS})}_2\text{L}_2 \ (L = \text{metz}, \text{mtbtz}) \]

From the ligand field spectrum of the cobalt dope of Zn(\text{NCS})_2\text{L}_2, it is clear that the metal ions are tetrahedrally surrounded. As in all other compounds presented so far, the thiocyanate groups in these two compounds are N-coordinating. Together with the composition of the compounds a mononuclear structure is proposed in which the ligands are monodentate. A similar structure has been reported for Zn(4-\text{R}-\text{butyl}-1,2,4-triazole)_2(\text{NCS})_2 [26]. It appeared impossible to prepare a cobalt dope of Zn(\text{NCS})_2\text{L}_2; adding cobaltchloride during the synthesis resulted in a sample, which showed different X-ray powder, and IR patterns and metal analyses (zinc analysis: 15.96\%, \( \nu_{\text{CN}} \): 2080 cm\(^{-1}\) instead of 2090 cm\(^{-1}\)).

\[ [\text{Cd}_2(\text{NCS})_4\text{L}_3] \ (L = \text{metz, mtbtz}) \]

These two cadmium compounds show remarkable differences in the thiocyanate IR vibrations as compared with the other compounds reported now. The \( \nu_{\text{CN}} \) absorptions appeared at 2100, 2060 and 1990 cm\(^{-1}\), whereas the \( \nu_{\text{CS}} \) absorptions for the mtbtz compound have been observed at 792, 772 and 751 cm\(^{-1}\). Due to a ligand vibration at 790 cm\(^{-1}\) in the metz compound, only a \( \nu_{\text{CS}} \) at 750 cm\(^{-1}\) could be observed.

The \( \nu_{\text{CN}} \) vibration at 2100 cm\(^{-1}\) and the \( \nu_{\text{CS}} \) at 751 cm\(^{-1}\) can be ascribed to a N, S bridging thiocyanate in agreement with the absorptions observed for [Cd(\text{NCS})_2(6,8-\text{dimethyl}[1,2,4]\text{triazolo[3,4-b]}\text{pyridazine})_2]_x at 2095, 2105 and 764 cm\(^{-1}\) resp. [27, 28]. The absorptions at 1990 and 792 cm\(^{-1}\) indicate bidentate N bridging thiocyanate as observed in [Cd(\text{NCS})_2(4-\text{tert-butyl}-1,2,4-triazole)_1]_x [4]. The \( \nu_{\text{CN}} \) vibration at 2060 and 772 cm\(^{-1}\) are described to N-monodentate thiocyanate [4, 15, 16]. The coordination of sulfur also appeared from the UV/visible spectrum of the Cu dope of [Cd(\text{NCS})_2(\text{mtbtz})]_x showing charge-transfer bands at 20.2 and 27.2·10^3 cm\(^{-1}\), most likely arising from Cu–S bonds.

It is quite clear that in compounds with a metal:ligand ratio equal to 4:5 all ligands have to be bidentate. Beside that six bidentately coordinating thiocyanate anions must be present in order to get six-coordinated metal ions. It is very likely to assume six coordination around Cd, because of the ESR spectrum of the copper dope of [Cd(\text{NCS})_2(\text{mtbtz})]_x, which showed an axial spectrum with \( g_s = 2.05, \ A_N = 17 \text{ G} \) (only observed at 77 K), \( g_{||} = 2.28 \) and \( A = 175 \text{ G} \).

Combining the now available results, a chain-like structure can be proposed for these compounds. However, it is not possible to derive conclusions about the number of N, S and N bridging thiocyanate, neither about which types of bridges are linking each pair of Cd ions.

**Final Remarks**

The compounds obtained with these asymmetric ligands and NCS\(^{-}\) as anion show similarity with the compounds obtained with symmetric 4-alkylsubstituted triazoles, as also appeared to be the case for the trifluoromethanesulfonate compounds [1]. Using 4-R-1,2,4-triazole (\( R = \) methyl, ethyl, allyl and phenyl) dinuclear compounds have been reported [3, 8, 20, 21]; the same structure is proposed for the compounds reported now. The magnitude of the metal–metal interactions lie in the same range as observed for the compounds with symmetric triazoles, which in retrospect could be expected from the great similarity between the compounds.
It is quite clear from the results described above and elsewhere [1–10, 20, 21], that the structure of the compounds obtained with non-chelating triazole ligands, mainly depends on the used anion. Using anions, such as NCS\(^-\), in many cases leads to the formation of dinuclear compounds with coordinated anions, whereas non-coordinating anions, such as trifluoromethanesulfonate, result in trinuclear compounds with other ligands as monodentate end groups. The thiocyanate anion clearly stops chain growing more effective than solvent molecules do. As has been argued above, the M(II)(NCS)_2 compounds obtained with 3 moles of metz and mtbtz are asymmetric by definition. This means that different coordination sites are present in the compounds. It is worthwhile to spend some effort on the synthesis of heteronuclear compounds, exploiting the un-equivalency of the coordination sites.

This work was sponsored by the Leiden Materials Science Centre (Werkgroep Fundamenteel Materielenonderzoek). The present investigations were carried out with support from the Netherlands Foundation for Chemical Research (SON) and with financial aid from the Netherlands Organization for Pure Research (ZWO) through project 11–28–17.