Complexes of 1,2,4-Triazoles, Part XVI
Binuclear Complexes of Transition Metal(II)thiocyanates
with 4-Ethyl-1,2,4-triazole

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4-Ethyl-1,2,4-triazole, Ligand Field, Magnetic Exchange, Binuclear Complexes

Coordination compounds of 4-ethyl-1,2,4-triazole (Ettrz) with Mn, Fe, Co, Ni, Cu and Zn are reported. The compounds have been identified and characterized by chemical analyses, infrared and ligand field spectra, electron paramagnetic resonance (e.p.r.) measurements, magnetic susceptibility measurements and thermoanalytical experiments. Except for the Cu compound, which is polynuclear, all compounds appear to be binuclear, with both bridging bidentate and non-bridging triazole ligands. The overall formula is M(Ettrz)₂(NCS)₂(H₂O)₃/2 for Mn, Fe, Co and Ni. The copper and zinc compounds have the formula Cu(Ettrz)₂(NCS)₂ and Zn(Ettrz)₂(NCS)₂.

Introduction

Complexes of 4-substituted 1,2,4-triazoles have attracted some interest in recent years, since it has been claimed, that this kind of compounds can be active in the control of phytopathogenic fungi [1, 2]. The first examples of such compounds were reported in the patent literature [1, 2]. As found in preliminary experiments, the existence of some of the reported compounds [1, 2] is questionable.

Detailed investigation on the coordination chemistry of unsubstituted 1,2,4-triazole showed the occurrence of complicated structures, in which triazole is bridging with its 2,4-N donor atoms [3, 4]. Blocking the 4-position by an alkyl substituent forces the triazole nucleus to bind in a bidentate, bridging way, which is of great interest for the study of the magnetic exchange between the ligand-bridged transition metal ions. Initial experiments showed, that with 4-Metz a binuclear compound could be isolated, which appeared to have three bidentate bridging 4-Metz ligands [5].

Previous work has shown, that thiocyanates are very useful starting materials for triazole coordination compounds [3]. Therefore, the present paper deals with transition-metal thiocyanates coordinated by 4-ethyl-1,2,4-triazole, abbreviated Ettrz.

A related paper will deal with compounds FeCl₃(4-R-trz)₃, which have polynuclear structures [6].

Experimental

Ettrz was prepared according to Bayer [1, 2]. A stream of EtNH₂, mixed with N₂, was passed into a refluxing solution of monoformyl hydrazine and HC(OEt)₂ in EtOH. Commercially available metal salts were used without further purification. The metal coordination compounds were prepared according to the following methods:

Preparation method A

Metal nitrate (5 mmol) was dissolved in H₂O (ca. 15 ml). A solution of NH₄SCN (10 mmol) in H₂O (15 ml) was added rapidly. Ettrz (10 mmol), dissolved in H₂O (10 ml), was added slowly to the boiling solution of the metal salt. The complex crystallized after standing for several days.

Preparation method B

This preparation method is analogue to method A, with only a small modification. Prior to the addition of Ettrz, the metal salt solution was acidified with a few drops of nitric acid.

Preparation method C

Freshly prepared metal thiocyanate (5 mmol) was mixed with 50 ml of Me₄CO. Ettrz (10 mmol) in Me₄CO (20 ml) was added rapidly to the boiling solution of the metal salt. The compound crystallized upon standing.

Preparation method D

NH₄SCN (10 mmol) was dissolved in H₂O (15 ml). After leading SO₂ for 2 min through the solution, Fe(NH₄)₂(SO₄)₃ • 6H₂O (5 mmol) was added rapidly. Then Ettrz (10 mmol) in H₂O (10 ml) was added slowly to the hot metal salt solution. Crystallization occurred while standing for several days.

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Metal analyses were carried out by complexometric titration after prior decomposition by heating in nitric acid. C, H and N analyses were carried out by the Pascher Analytic Laboratory in Bonn, W-Germany. The ligand field spectra were recorded on a Beckman DK-2A UV-VIS spectrophotometer (350–2000 nm), diffuse reflectance method, with MgO as a reference. The infrared spectra were recorded on a Perkin Elmer 580 spectrophotometer (4000–180 cm⁻¹) as nujol mulls. Thermoanalytical experiments were carried out on a Mettler Vacuum Thermal Analyser TA-1. The compounds were heated up to 200 °C at a rate of 4 °C/min under N₂ atmosphere. e.p.r. spectra of powdered Cu samples were recorded on a Varian 4502 apparatus, equipped with a Varian 4531 multipurpose cavity, employing a 100 kHz field modulation, at the Chemistry Department, University of Fribourg, Switzerland. Magnetic susceptibility measurements between 80 and 300 K were carried out using a PAR vibrating sample magnetometer model 150 A with Janis cryostat. X-ray powder diffractograms were obtained on a Philips Powder Diffractometer.

Results and Discussion

General

The obtained complexes are listed in Table I, together with their preparation methods, analyses and other relevant properties. The several compounds will be discussed subsequently. In the past infrared spectroscopy has often proved to be a powerful tool in predicting the coordination modes of 1,2,4-triazoles [3, 8]. Between 600 cm⁻¹ and 700 cm⁻¹ two out of plane ring-vibrations are infrared active for 1,2,4-triazole with C₄ᵥ-symmetry. Absence of one of these vibrations is an evidence for local C₂ᵥ-symmetry of the 1,2,4-triazole [3, 8]. The Et-substituent on the 4-position of the triazole ring makes the spectrum more complicated, as the ring-Et stretching vibration also appears in the region of 600–700 cm⁻¹. The totally symmetric ring-Et stretching was distinguished from the ring torsion vibration by the high intensity of its Raman line and assigned to the 665 cm⁻³ frequency absorption. The remaining absorptions in the infrared spectrum between 600 cm⁻¹ and 700 cm⁻¹ may now be assigned to the ring torsions of the triazole ring.

Tab. I. Analytical data, colours, diffraction types and melting points of coordination compounds containing Ettrz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>prep.</th>
<th>Diff. type</th>
<th>colour</th>
<th>Elemental analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(Ettrz)₂(NCS)₂(H₂O)₃/2</td>
<td>A</td>
<td>a</td>
<td>colourl.</td>
<td>M [%]</td>
</tr>
<tr>
<td>Fe (Ettrz)₂(NCS)₂(H₂O)₃/2</td>
<td>D</td>
<td>a</td>
<td>white</td>
<td>14.5 (14.0)</td>
</tr>
<tr>
<td>Co (Ettrz)₂(NCS)₂(H₂O)₃/2</td>
<td>A</td>
<td>a</td>
<td>red</td>
<td>14.9 (14.9)</td>
</tr>
<tr>
<td>Ni (Ettrz)₂(NCS)₂(H₂O)₃/2</td>
<td>B</td>
<td>a</td>
<td>blue</td>
<td>15.0 (15.0)</td>
</tr>
<tr>
<td>Cu (Ettrz)₂(NCS)₂</td>
<td>C</td>
<td>b</td>
<td>green</td>
<td>17.3 (17.0)</td>
</tr>
<tr>
<td>Zn (Ettrz)₃/2(NCS)₂</td>
<td>A</td>
<td>c</td>
<td>white</td>
<td>19.6 (19.4)</td>
</tr>
</tbody>
</table>

Calculated values in parentheses.
Table II. Metal-nitrogen absorptions (cm\(^{-1}\)) of coordination compounds containing Ettrz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>235 (vs) 215 (s, sh)</td>
</tr>
<tr>
<td>Fe((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>232 (vs)</td>
</tr>
<tr>
<td>Co((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>270 (vs)</td>
</tr>
<tr>
<td>Ni((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>278 (vs)</td>
</tr>
<tr>
<td>Cu((\text{Ettrz})_2\text{(NCS)}_2)</td>
<td>320 (vs) 271 (vs) 246 (w)</td>
</tr>
<tr>
<td></td>
<td>223 (s) 202 (w, sh) 196 (m)</td>
</tr>
<tr>
<td>Zn((\text{Ettrz})_3\text{(NCS)}_2)</td>
<td>335 (s) 320 (s) 233 (vs)</td>
</tr>
</tbody>
</table>

The e.p.r. spectrum is in agreement with a distorted elongated octahedral coordination around Cu(II), having a \(g_{||}\) of 2.24 and a \(g_{\perp}\) of 2.05. Hyperfine splittings remain unresolved, since the magnetic exchange between the Cu(II) ions is large compared to the (super)-hyperfine interactions [12].

The structure complying with the results of these experiments, is a polynuclear chain, in which the Cu ions are linked by a double bridge of 1,2-bi-coordinating Ettrz and wherein the isothiocyanates are coordinated monodentately. Because of steric reasons the arrangement will be cis rather than trans. The symmetry ruling the C–H out of plane vibration is then low enough to give two different C–H out of plane vibrations (890, 862 cm\(^{-1}\)).

The observed 6 Cu–N vibrations (Table II) in the far-infrared region are in agreement with this exception. Although rather unlikely, a trans geometry with different Cu–N distances may not be excluded completely. Magnetic susceptibility measurements in the 80–300 K region delivered the MU and \(\theta\) values, which are listed in Table IV. The value \(\theta = -3.7\) K, obtained from the data between 80 K and 300 K is apparently unreliable, as susceptibility measurements from 1.8–4.2 K yielded \(\theta \simeq -0.2\) K. The value of the exchange constant can be estimated by means of the molecular field approximation \(\theta = 2 J S(S+1)/3k\), when \(Z\) is the number of magnetic neighbours. For a magnetic polynuclear chain, \(Z = 2\), hence \(J/k = -0.2\) K. In that case, the \(\chi vs T\) curve should exhibit a maximum at \(T \simeq 0.2\) K, which is outside the range that can be obtained with our equipment. Therefore it was not possible to verify the proposed structure with magnetic susceptibility measurements.

The weak spin exchange between the Cu(II)-ions is again a strong indication for a cis geometry of the compound.

\(\text{Zn(Ettrz)}_3\text{(NCS)}_2\)

Even when a ratio \(\text{MX}_2\) to \(\text{L}\) of 1:7 was used in the preparation, the Zn-compound crystallized with overall formula \(\text{MX}_3\text{L}_{3/2}\).

From the infrared spectrum it was concluded, that part of the NCS-groups are coordinating through the nitrogen, while the remaining ions are not coordinating but ionic (v(CN) at 2100 and 2050 cm\(^{-1}\)).

Table III. Ligand filed data of coordination compounds containing Ettrz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ligand field bands ([10^6\text{ cm}^{-1}])</th>
<th>Dq ([\text{cm}^{-1}])</th>
<th>B ([\text{cm}^{-1}])</th>
<th>Dq/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>11.6 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>9.9 (s) 16.7 (sh) 20.6 (s)</td>
<td>1085</td>
<td>795</td>
<td>1.36</td>
</tr>
<tr>
<td>Ni((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>10.9 (s) 17.7 (s)</td>
<td>1090</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>Cu((\text{Ettrz})_2\text{(NCS)}_2)</td>
<td>15.4 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* \(\nu_3\) is not observed in the ligand field spectrum. Calculation of B, based on \(\nu_1\) and \(\nu_2\) yields an unreliable value for this parameter.

Table IV. Magnetic data from Faraday and PAR experiments of coordination compounds containing Ettrz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MU (BM)</th>
<th>(\theta) (K)</th>
<th>(J) (cm(^{-1}))</th>
<th>(\chi_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>5.88</td>
<td>-7.1</td>
<td>-0.72</td>
<td>3.0</td>
</tr>
<tr>
<td>Fe((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>5.53</td>
<td>-7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>5.15</td>
<td>-13.9</td>
<td>-12.11*</td>
<td>12.7</td>
</tr>
<tr>
<td>Ni((\text{Ettrz})_2\text{(NCS)}_2\text{(H}_2\text{O})_3/2)</td>
<td>3.13</td>
<td>-29.9</td>
<td>-9.54</td>
<td>29.0</td>
</tr>
<tr>
<td>Cu((\text{Ettrz})_2\text{(NCS)}_2)</td>
<td>1.86</td>
<td>-3.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Based on the prediction for Ising dimers with \(s = 1/2\).
The i.r. spectrum between 600 cm\(^{-1}\) and 700 cm\(^{-1}\) indicates that there are Ettrz groups coordinating bidentately as well as monodentately. The out of plane absorption around 640 cm\(^{-1}\) is split up (629, 634, 644 cm\(^{-1}\)). The lower doublet may be assigned to the out of plane vibration of the bridging ligands, while the absorption at 644 cm\(^{-1}\) belongs to Ettrz coordinating by only one N atom. The presence of the weak second out of plane vibration at 683 cm\(^{-1}\) confirms the presence of monodentately coordinating Ettrz. The splitting of the C-H out of plane vibration (892 (s), 882 (sh), 875 (m) cm\(^{-1}\)) is also a strong indication for the presence of two different binding modes of the ligand.

Therefore a binuclear structure with a double bridge of 1,2-bicoordinating Ettrz between the Zn ions was concluded (Fig. 1). The four coordination around the metal ions is completed by an Ettrz coordinating monodentately and thiocyanates coordinated through the nitrogen. A further indication for the proposed structure arises from the far-infrared data (Table II). The coordination number of the metal is decreased, the \(\nu(M-NCS)\) increases [13]. The \(\nu(M-NCS)\) in this compound is found at 320 cm\(^{-1}\) and 335 cm\(^{-1}\), which is very high compared to the other, octahedral, complexes. Because we did not succeed so far in preparing single crystals of this compound, it was not possible to verify the proposed structure with X-ray single crystal measurements.

\[
M(Ettrz)_2(NCS)_3(H_2O)_{3/2} \\
(M = Mn, Fe, Co and Ni)
\]

The infrared spectra of the X-ray isomorphous Mn, Fe, Co and Ni compounds are nearly identical.

In the 600–700 cm\(^{-1}\) region, the absorptions of both out of plane ring vibrations are observed. The lower of these is found at 640 cm\(^{-1}\) and has a high intensity. The other absorption is located at 680 cm\(^{-1}\) and is weak in all complexes. The presence of it can be explained by the presence of a certain amount of ligands, coordinated monodentately to the metal ion. The coordination of these triazole rings by only one metal atom lowers the symmetry enough to activate the forbidden ring torsion. In the infrared spectra \(\nu(CS)\) is found around 800 cm\(^{-1}\). The assumption, that the NCS-groups coordinate via the nitrogen, is again confirmed by the position of \(\nu(CN)\) (2100 cm\(^{-1}\)). The OH-stretching vibration at 3400 cm\(^{-1}\) exhibits a shoulder at 3645 cm\(^{-1}\) and the OH-bending (1655 cm\(^{-1}\)) shows a shoulder at 1615 cm\(^{-1}\). This suggests, that different kind of H\(_2\)O molecules are present in these compounds.

The far-infrared data are listed in Table II. No clear M–O vibrations could be observed.

As an example, the infrared spectrum of Mn(Ettrz)\(_2\)(NCS)\(_2\)(H\(_2\)O)\(_{3/2}\) is showed in Fig. 2.

The ligand field spectra of the Fe, Co and Ni compounds are in agreement with octahedrally coordinated metal ions. The ligand field bands, together with the calculated Dq and B values are listed in Table III. The ligand field spectrum of Fe(Ettrz)\(_2\)(NCS)\(_2\)(H\(_2\)O)\(_{3/2}\) shows, that at room temperature the compound is in the high spin state.

The conclusion, based on the infrared data, that part of the H\(_2\)O molecules are coordinated to the metal ions, is supported by the results of thermo-analytical measurements. On heating (or heavy powdering) the Co compound showed a transition in color from red to blue, which apparently is due to a change in coordination from octahedral to tetrahedral. Co(Ettrz)\(_2\)(NCS)\(_2\)(H\(_2\)O)\(_{3/2}\) has been used in thermo-analytical experiments. 15.4 mg of this compound was heated up to 200 °C at a rate of 4 °C/min under nitrogen atmosphere. The d.t.g. and d.t.a. curves are shown in Fig. 3. The d.t.a. curve displays 2 first order phase transitions, whereby the second is not accompanied by a loss of weight. A decrease in weight of 1.0 mg or 6.5% is in agreement with a loss of 3/2 H\(_2\)O. Based on the observation, that the change in coordination occurs in combination with a loss of H\(_2\)O, the conclusion, that part of the H\(_2\)O molecules are coordinated to the metal ions, seems to be justified. It is also to be expected,
that hydrogen bonding plays an important role in the stability of this compound.

Magnetic susceptibility data in the range of 2–300 K were collected for the Mn, Co and Ni compounds. The Fe compound was measured from 80–300 K. In the region of 80–300 K the susceptibilities follow a Curie-Weiss behaviour.

The data collected from the magnetic susceptibility measurements are listed in Table IV. The rather high MU value (5.16 BM) for the Co compound may be caused by preferred orientation of the crystals. The MU value of Fe(Ettrz)$_2$(NCS)$_2$(H$_2$O)$_{3/2}$ (5.53 BM) confirms the conclusion based on the ligand field spectrum, that high-spin Fe(II) is present.

The susceptibilities of the Mn, Co and Ni compounds show maxima at 3.0 K, 12.7 K and 29.0 K respectively. The susceptibilities of the Mn and Ni
compounds were fitted by means of least-squares methods to formulae for dimers with isotropic interaction with $S = 5/2$ and $S = 1$ respectively [14]. The susceptibility data for the Ni compound are shown in Fig. 4. A good fit is obtained with $J = -9.54 \text{ cm}^{-1}$ and $g = 2.15$ (solid curve Fig. 4). For Mn(Ettrz)$_2$(NCS)$_2$(H$_2$O)$_3/2$ a fair fit was obtained with $J = -0.72 \text{ cm}^{-1}$ and $g = 2.00$.

For the Co compound the situation is more complicated, since the orbital moment is only partly quenched. The combined action of the low-symmetry ligand field and the spin-orbit coupling results in the splitting of the lowest orbital triplet ($^4T_{1g}$) into six Kramers doublets. When it is assumed, that the distance between the lowest doublet and the nearest higher energy level is large compared with the exchange constant, the magnetic properties can be described in terms of an effective spin $s' = 1/2$, with anisotropic $g$-values. Since the anisotropy of the $g$-tensor is not known, we have compared the susceptibilities of the Co compound with the prediction for Heisenberg and Ising dimers with $s = 1/2$. The susceptibilities are given by

$$
\chi_H = \frac{N g^2 \mu_B}{kT} \cdot \frac{1}{3 + \exp(-2J/kT)}
$$

and

$$
\chi_I = \frac{N g^2 \mu_B^2}{kT} \cdot \frac{1}{1 + \exp(-J/kT)}
$$

[15, 16].

Fig. 5 shows the data and the fit to the Ising model (solid curve, $J = -12.11 \text{ cm}^{-1}, g = 6.79, \chi_{\text{TIP}} = 0.02$). The quality of the fit, provided by the Heisenberg model was about the same ($J = -7.54 \text{ cm}^{-1}, g = 3.38, \chi_{\text{TIP}} = 0.02$). The fits are rather poor, so that the values of $J$, $g$ and $\chi_{\text{TIP}}$ must be regarded as estimates only. The misfit for $T < 8 \text{ K}$ may be due to a neglect of $\chi_I$ and to paramagnetic impurities [17]. As mentioned before, the compound turns blue on powdering. Therefore the crystallites were slightly compressed into the sample holder of the vibrating sample magnetometer, without powdering them. As a result a small amount of the “blue” phase may have been formed, which is most likely paramagnetic, and anyway has a much smaller magnetic moment than octahedrally coordinated Co(II).

Obviously, single-crystal susceptibility measurements are necessary to study this problem more satisfactorily. In this case it is possible to use fit models, proposed by Gerloch et al. [18, 19], which would probably provide a better fit. However, attempts to obtain large single-crystals remained unsuccessful so far.

The results of magnetic susceptibility measurements strongly suggest, that either linear chains of bridged M(II) ions are present or that the compound
is built up of linear clusters containing an even number of M(II) atoms. Based on infrared data and on stoichiometric grounds a dimeric structure is thought to be the most acceptable possibility. In the proposed structure two metal ions are bridged by three Ettrz groups. The octahedra around the metal ions are completed by N-donating NCS groups, an Ettrz coordinating by only one N atom and a coordinated H$_2$O molecule.

In order to verify this assumption a crystal structure determination of Ni(Ettrz)$_2$(NCS)$_2$(H$_2$O)$_3/2$ was undertaken. The results of which will be dealt with in a further communication [20].

Conclusions

Infrared data and magnetic susceptibility measurements provided strong indication for a binuclear structure for the compounds M$_2$(Ettrz)$_4$(NCS)$_4$(H$_2$O)$_3$ with M = Mn, Fe, Co and Ni. In these compounds one Ettrz acts as a monodentate ligand, while the other three Ettrz units are coordinated 1,2-bidentate to the metal ions. Antiferromagnetic interactions exist in the dimeric Mn, Co and Ni complexes. For Cu(Ettrz)$_2$(NCS)$_2$ a poly-nuclear structure is very likely. The Ettrz molecules act as bidentate ligands and the NCS-groups are N-donors. For Zn(Ettrz)$_3/2$(NCS)$_2$ a binuclear structure is proposed, in which Zn possesses a four coordination.

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