Syntheses, Crystal Structures and Magnetic Properties of
Cr(NCNH$_2$)$_4$Cl$_2$ and Mn(NCNH$_2$)$_4$Cl$_2$

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The two isotypic compounds Cr(NCNH$_2$)$_4$Cl$_2$ and Mn(NCNH$_2$)$_4$Cl$_2$ have been synthesized and characterized by X-ray diffraction. They crystallize in the cubic space group $\text{Im} \bar{3} \text{m}$ ($Z = 6$) with $a = 12.643(2)$ Å for Cr(NCNH$_2$)$_4$Cl$_2$ and $a = 12.821(1)$ Å for Mn(NCNH$_2$)$_4$Cl$_2$. The divalent transition metal ions are octahedrally coordinated by four H$_2$NCN molecules in equatorial and two chloride ions in axial positions. The magnetic susceptibility data of the four Curie-paramagnetic compounds Cr(NCNH$_2$)$_4$Cl$_2$, Mn(NCNH$_2$)$_4$Cl$_2$, Co(NCNH$_2$)$_4$Cl$_2$, and Ni(NCNH$_2$)$_4$Cl$_2$ have been analyzed in greater detail, including many-body quantum theory.

**Key words:** Chromium, Manganese, Cyanamide, Chloride, Crystal Structure, Magnetism

**Introduction**

In the course of transition metal cyanamide research, the crystal structures and magnetic properties of Fe(NCNH$_2$)$_4$Cl$_2$, Co(NCNH$_2$)$_4$Cl$_2$, Ni(NCNH$_2$)$_4$Cl$_2$, and Cu(NCNH$_2$)$_4$Cl$_2$ have already been communicated [1 – 3]. The chemical similarity of the NCN$^2-$ anion with O$_2$ is obvious, and so is the one between H$_2$NCN and H$_2$O. The complete series of aquo-chloro complexes of the general form $M$(OH)$_2$$_4$Cl$_2$ ($M = Cr, Mn, Fe, Co, Ni) [4 – 8] is already known. To close the cyanamide series, the two compounds Cr(NCNH$_2$)$_4$Cl$_2$, 1, and Mn(NCNH$_2$)$_4$Cl$_2$, 2, have been synthesized. Below, we report on their crystal structures and magnetic properties in more detail.

**Results and Discussion**

The X-ray crystal-structure analyses of 1 and 2 were performed based on single-crystal (Mn compound) and powder (Cr compound) diffraction data, respectively. The observed and calculated diffraction patterns of 1 are shown in Fig. 1. As expected, the structure is isotypic with $M$(NCNH$_2$)$_4$Cl$_2$ ($M = Fe, Co, Ni and Cu).

![Fig. 1. Observed (circles), calculated (line), and difference (below) X-ray diffraction intensities of Cr(NCNH$_2$)$_4$Cl$_2$. The vertical markers show the positions of the Bragg reflections.](image-url)

**Structure**

The environment of the metal atom and the crystal structure of $M$(NCNH$_2$)$_4$Cl$_2$ ($M = Cr, Mn, 2$) are depicted in Figs. 2 and 3, respectively. Each $M^{2+}$ ion...
Table 1. Selected bond lengths (Å) and bond angles (deg) of all 3d transition metal tetracyanamide dichlorides, $M\text{-}NCNH_2\text{Cl}_2$, with standard deviations in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Cr(4)</th>
<th>Mn(4)</th>
<th>Fe(4)</th>
<th>Co(4)</th>
<th>Ni(4)</th>
<th>Cu(4)</th>
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<tbody>
<tr>
<td>M–N1</td>
<td>4 × 2.065(9)</td>
<td>4 × 2.208(3)</td>
<td>4 × 2.090(3)</td>
<td>4 × 2.048(3)</td>
<td>4 × 2.037(4)</td>
<td></td>
</tr>
<tr>
<td>M–Cl</td>
<td>2 × 2.745(4)</td>
<td>2 × 2.588(14)</td>
<td>2 × 2.516(1)</td>
<td>2 × 2.483(1)</td>
<td>2 × 2.783(1)</td>
<td></td>
</tr>
<tr>
<td>C–N1</td>
<td>1.09(2)</td>
<td>1.114(4)</td>
<td>1.125(5)</td>
<td>1.121(4)</td>
<td>1.121(4)</td>
<td>1.047(7)</td>
</tr>
<tr>
<td>C–N2</td>
<td>1.34(1)</td>
<td>1.336(5)</td>
<td>1.323(9)</td>
<td>1.331(5)</td>
<td>1.327(5)</td>
<td>1.343(12)</td>
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<tr>
<td>N2–H</td>
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<td>0.86(3)</td>
<td>0.85(4)</td>
<td>0.87(3)</td>
<td>0.93(3)</td>
<td>0.98(5)</td>
</tr>
<tr>
<td>M–N1–C</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>N1–C–N2</td>
<td>164.1(3)</td>
<td>165.4(5)</td>
<td>166.5(10)</td>
<td>166.2(5)</td>
<td>166.2(4)</td>
<td>167.4(16)</td>
</tr>
<tr>
<td>C–N2–H</td>
<td>113.0(6)</td>
<td>109.3(17)</td>
<td>110.9(4)</td>
<td>111.2(3)</td>
<td>113(2)</td>
<td>120(3)</td>
</tr>
</tbody>
</table>

is octahedrally coordinated by four nitrogen-bonded cyanamide molecules in equatorial positions and two chloride ions in axial positions. The selected bond lengths and angles of 1 and 2 are compared with those of the already reported members of the series in Table 1.

The Mn–N1 distances in 2 are 2.200(3) Å and slightly shorter than those in Mn(NH$_3$)$_2$Cl$_2$ (2.270(3) Å) [9]. The Mn–Cl distances amount to 2.588(14) Å, somewhat longer than those in octahedral MnCl$_4$ units (2.548(2) Å) [10]. It seems that the Mn–N1 and the Mn–Cl distances agree well with the sum of the effective (high-spin) ionic radii (2.29 Å and 2.64 Å) [11].

For Cr(4) and Mn, the Cr–N1 and the Cr–Cl distances amount to 2.065(9) and 2.745(4) Å, respectively. On comparison with other isotypical complexes (Table 1), the Cr–N1 distance appears rather normal. The Cr–Cl distance is in very good agreement with published data such as 2.758(9) Å in Cr(H$_2$O)$_4$Cl$_2$ [4]. The somewhat larger value compared to the sum of effective (high-spin octahedral) ionic radii (2.61 Å) [11] is due to the $d^3$ chromium(II) ion with a high-spin electronic configuration $(t_{2g})^3(e_g)^1$. Similar findings, e.g., Cr–Cl = 2.40 Å (4×) and 2.91 Å (2×), are known from CrCl$_2$ [12].

The two C–N bond lengths of the cyanamide ligands suggest a triply bonded C–N1 = 1.09(2) Å and a singly bonded C–N2 = 1.34(1) Å for 1, as do C–N1 = 1.114(4) Å and C–N2 = 1.336(5) Å for 2. These interatomic distances are consistent with those (1.15 and 1.31 Å) in pure molecular cyanamide (H$_2$NCN) [13]. While the N1–C–N2 angles are 164.1(3)$^\circ$ for 1 and 165.4(5)$^\circ$ for 2, the N2–H bond lengths underestimated by the X-ray method are 0.91(1) Å for 1 and 0.86(3) Å for 2. Fig. 3 indicates that each H$_2$NCN molecule forms two hydrogen bonds to Cl– which functions as a four-proton acceptor. The
The molecular-field parameter. The quantum numbers of $B$ and $2$ represent the single-center susceptibility and the crystal/ligand-field parameters, respectively. The term $\lambda$ is represented by $2.0$ and accounts for the following single-ion contributions in the case of $\text{Cr}^{2+}$, $\text{Co}^{2+}$, and $\text{Ni}^{2+}$ and, second, antiferromagnetic coupling between the magnetic ions within a given three-dimensional network for all compounds [14].

All the magnetic data were analyzed by using the program CONDON 2.0 [15] with the complete basis set as a function of the applied field ($B = 0.1, 0.5$, and $1.0$ T), which is necessary to yield reliable information on the magnetic dipole orientation with respect to the $D_{4h}$ local symmetry of the metal ion. CONDON 2.0 takes into account the following single-ion effects: ligand-field effects ($H_{lf}$), interelectronic repulsion ($H_{ee}$), spin-orbit coupling ($H_{so}$), and the applied field ($H_{mag}$). Generally, for a magnetically isolated $3d^n$ metal ion in a ligand-field (lf) environment exposed to an external magnetic field $B$, the Hamiltonian of the metal ion [16, 17] is represented by

$$H = H_{ee} + H_{lf} + H_{so} + H_{ex} + H_{mag}.$$ 

This expression can be considered as an extension of the EHCF $d$-shell Hamiltonian [18] on account of the spin-orbit interaction operator $H_{so}$ and the operator describing the interaction with the applied magnetic field $H_{mag}$. Fig. 4 shows the experimental magnetization ($\mu_{\text{eff}}, \text{SI units}$; $\mu_{\text{eff}} = 797.74, \sqrt{\chi_{m}T}$) of $1$, $2$, $3$, and $4$ within the temperature range $2 – 290$ K. This data set was fitted to the above-stated Hamiltonian using the ligand-field effect, spin-orbit coupling, and exchange coupling. The values for the spin-orbit coupling parameter and Racah parameters were chosen on the basis of the optical spectra and are consistent with our EHCF calculations [18].

The exchange interactions between the metal ions are taken into account in the molecular field approximation

$$\chi_{m}^{-1} = \chi_{m}^{-1}(B, C, \zeta, B_{q}) - \lambda_{\text{mf}},$$

where $\chi_{m}^{-1}$ represents the single-center susceptibility and $\lambda_{\text{mf}}$ the molecular-field parameter. The quantities $B_{q}$ represent the crystal/ligand-field parameters in Wybourne notation ($B_{0}^{0}, B_{0}^{4}$, and $B_{4}^{4}$ for a distorted octahedral coordination environment) according to

$$B_{q}^{0} = \sum_{i=1}^{N} C_{0}^{0}(i) + \sum_{i=1}^{N} C_{4}^{0}(i) + \sum_{i=1}^{N} C_{4}^{4}(i)$$

where $C_{0}^{0}(i)$ and $C_{4}^{4}(i)$ are the Racah tensor components describing the angular dependence of the ligand field. The $B_{q}^{0}$ ligand-field parameters can be determined by the EHCF procedure [18].

At room temperature, the effective Bohr magneton number of $2$ is roughly $5.9$ per $\text{Mn(NCNH}_{2})_{4}\text{Cl}_{2}$ unit or per high-spin $\text{Mn}^{2+}$ ion, a value that corresponds to the spin-only value of $5.92$ (see Fig. 4). The $\chi_{m}^{-1}$ vs. $T$ plot reveals a linear behavior between $25$ and $290$ K. 

![Fig. 4. Temperature dependence of $\mu_{\text{eff}}$ in $\mu_{B}$ of $1$, $2$, $3$, and $4$ at applied fields of $B = 0.1, 0.5$, and $1$ Tesla; see also text.](image-url)
This observation is supported by a linear fit of the reciprocal molar susceptibility to the Curie law above 25 K, leading to $C = 5.469 \times 10^{-5}$ m$^3$ K mol$^{-1}$ with $\mu_{so} = 5.9$ $\mu_B$ and a Weiss temperature $\theta = -0.3$ K.

An octahedral ligand field would generate, in the case of Ni$^{2+}$, an orbital singlet $[4, 3d^8, 3A_2; \mu_{so} = 2.87 \mu_B]$, and an orbital doublet $[1, 3d^5, 5E; \mu_{so} = 4.90 \mu_B]$ ground state in the case of Cr$^{2+}$. The actual symmetry, however, is lower ($C_{4v}$) so that relative to this point group the symmetry notation changes to $^3B_1$ for Ni$^{2+}$ whereas, for Cr$^{2+}$, the orbital doublet splits and the ground state is $^3B_1$. Therefore, Curie paramagnetism is observed if exchange interactions and saturation effects do not have a significant influence. The room temperature value depends on the ligand-field strength and the mixing of excited states into the ground term via spin-orbit interaction in both cases. In the range $T = 25-300$ K, the $\mu_{eff}$ values for Cr$^{2+}$ ($\mu_{eff} = 4.74 \mu_B$) and Ni$^{2+}$ ($\mu_{eff} = 3.05 \mu_B$) are independent of the temperature. The Curie-Weiss fit in the linear range of the $\chi^{-1}$ vs. $T$ plot corresponds to $C = 3.531 \times 10^{-5}$ m$^3$ K mol$^{-1}$ and a Weiss temperature $\theta = -0.4$ K ($\mu_{so} = 4.74 \mu_B$) for Cr$^{2+}$, whereas one finds $C = 1.4298 \times 10^{-5}$ m$^3$ K mol$^{-1}$ and a Weiss temperature $\theta = -1.9$ K ($\mu_{so} = 3.05 \mu_B$) for Ni$^{2+}$. There is no deviation from the spin-only values, but the small negative Weiss temperature manifests antiferromagnetic exchange interaction in the three-dimensional network.

The magnetic behavior of Co$^{2+}$ $[3, 3d^7, \mu_{so} = 3.87 \mu_B]$ is completely different from that of the other central ions. At room temperature, the effective Bohr magneton number ($\mu_{eff}$) of 4.74 is significantly larger than the spin-only value because of the positive spin-orbit coupling term for ions after a half-filled 3d shell. There is no temperature-independent behavior in the $\mu_{eff}$ vs. $T$ plot. The monotonous decrease of $\mu_{eff}$ towards lower temperatures for Cr is explained by single-ion effects ($H_{eff}, H_{ex}, H_{so}$) with a spatially degenerate $4E$ ground state which results from the tetragonal deformation of the octahedral $^4T_1$ ground state.

For all four compounds, the fitting procedure employs starting values for the ligand-field parameters $B_{2g}^0$, $B_{4g}^0$, and $B_{4u}^0$ that are directly picked from the ECHF calculations. The parameters used for Ni and Co in the ECHF calculations have been taken from the literature [24, 25], as was also done for Mn [26]; the hopping scaling parameters $B_{ML}$ for $M = Cr$ and $L = N$ were also available [27]. Chlorine-containing compounds of

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cr</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
</tr>
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<tbody>
<tr>
<td>$d^8$</td>
<td>$d^2$</td>
<td>$d^6$</td>
<td>$d^0$</td>
<td>$d^8$</td>
</tr>
<tr>
<td>Free ion ground state</td>
<td>$^1D_2$</td>
<td>$^5g$</td>
<td>$^5F_2$</td>
<td>$^3F_2$</td>
</tr>
<tr>
<td>Ligand field ($\chi_n$)</td>
<td>$^3E_2$</td>
<td>$^5A_1$</td>
<td>$^5F_2$</td>
<td>$^3A_2$</td>
</tr>
</tbody>
</table>

Here are the results of the fitting procedures for the magnetic susceptibility data of 1-4.

$C$, 10$^{-3}$ m$^3$ K mol$^{-1}$

$\chi_{obs}$ = $\frac{\chi_{fit} - \chi_{cal}}{\chi_{fit}} \times 100\%$, where $Q = \sum_{i=1}^{n} \frac{|\chi_{obs}(i) - \chi_{cal}(i)|}{\chi_{fit}(i)}$.

Cr had not been calculated by the ECHF so far. Therefore, we estimated the hopping scaling parameter $B_{ML}^0$ for $M = Cr$ and $L = Cl$ to be 1.70 in order to reproduce the fitted value of the $B_{2u}^0$ parameter for 1. The best fit results of the magnetic parameters are given in Table 2, in good agreement with the ECHF values and the molecular field parameter $\lambda_{aff}$ indicating antiferromagnetic coupling. For the Co$^{2+}$ complex the orbital reduction factor $\kappa$ is equal to 0.75, nicely in line with data of Co complexes in the literature [28]. The ratios $B_{2u}^0/B_{4g}^0 = 0.53$ and $B_{4u}^0/B_{4g}^0 = 0.12$ were fixed at the values of the ECHF calculations.

The dotted lines in Fig. 4 illustrate the temperature dependence of $\mu_{eff}$ exclusively in terms of isolated single-ion and magnetic saturation effects, that is, in the complete absence of antiferromagnetic (AF) exchange coupling. Including AF interactions, the ligand-field overall splitting derived from this magnetochemical analysis corresponds well to spectroscopic data [19] on tetragonally distorted octahedral $M^{2+}$ ($M = Cr, Mn, Co, Ni$) complexes and is in line with our ECHF calculations. The symmetries and spins for the tetragonal ($C_{4v}$) group are also given in Table 2. The ECHF calculations for all four elements exhibit the splitting pattern of the $d$ levels as shown in Scheme 1:
with \( \varepsilon(xy) - \varepsilon(xz) < 0 \) for the calculated values of the effective crystal fields, which fully explains the observed magnetic behavior.

According to our EHCF calculation, the \( d^7 \) (Co) compound 3 in the high-spin state is a Jahn-Teller system for which one may expect a deformation lifting the degeneracy of the ground electronic state. It has been shown [29] that in an analogous series of the \( M(H_2O)_4Cl_2 \) compounds this very Jahn-Teller distortion does take place in the Co member of the series. Such behavior, however, is not found for the present cyanamide series, probably due to the stiffer network involving hydrogen bonds between quasi-molecular moieties.

**Experimental Section**

**Syntheses**

Single crystals of \( \text{Mn(NCNH}_2)_4\text{Cl}_2 \) were prepared by dissolving 1 mmol (161.87 g mol\(^{-1}\)) \( \text{MnCl}_2 \cdot 2\text{H}_2\text{O} \) and 4 mmol (42.04 g mol\(^{-1}\)) \( \text{H}_2\text{CN} \) in 10 mL distilled water. After very slow evaporation of the aqueous solution under normal atmosphere within a few weeks, colorless cubic crystals were obtained.

Powderous \( \text{Cr(NCNH}_2)_4\text{Cl}_2 \), 1, and \( \text{Mn(NCNH}_2)_4\text{Cl}_2 \), 2, were prepared by treating anhydrous \( \text{MCl}_2 \) (\( M = \text{Cr} \) or \( \text{Mn} \)) and \( \text{H}_2\text{CN} \) mixed in 1:4 ratio using an agate mortar at room temperature in a glove box. While the \( \text{Cr(NCNH}_2)_4\text{Cl}_2 \) powder is light blue, the \( \text{Mn(NCNH}_2)_4\text{Cl}_2 \) powder is pale pink. Both of them are sensitive to hydrolysis.

**X-Ray structure determination**

A colorless crystal of 2 was selected and mounted in a glass capillary with oil. The diffraction data were collected on an Bruker SMART APEX CCD area detector diffractometer with graphite-monochromatized MoK\(_\alpha\) radiation. The structure is isotypic with \( M(\text{NCNH}_2)_4\text{Cl}_2 \) (\( M = \text{Fe, Co, Ni and Cu} \)) and was refined by full-matrix least-squares on \( F^2 \) using the SHELXL97 program [20]. As found before, \( \text{N}_2 \) is distributed over two equal sites with 50% occupancy [2], a result of the pyramidal configuration of the \( \text{N}_2 \) atom. The positions of the hydrogen atoms were found from a difference Fourier map. Details about the crystal data and data collection are summarized in Table 3. Tables 4 and 5 give positional and isotropic as well as anisotropic displacement parameters.

The structural characterization of powderous 1 was carried out at room temperature using a Stoe STADI MP diffractometer in transmission geometry with strictly monochromatized CuK\(_\alpha1\) radiation and a linear position-sensitive detector (PSD) with a flat-sample holder; the range of measure-
Table 4. Positional and isotropic displacement parameters (Å²) for Mn(NC NH₂)₄Cl₂ with standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>12e</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>Cl</td>
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<td>0</td>
<td>0.0298(14)</td>
<td>0.0724(4)</td>
</tr>
<tr>
<td>N1</td>
<td>1</td>
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</tr>
<tr>
<td>C</td>
<td>1</td>
<td>0.31720(18)</td>
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<td>0.31720(18)</td>
</tr>
<tr>
<td>N2</td>
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<td>0.0263(8)</td>
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<tr>
<td>H</td>
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<td>0.186(2)</td>
<td>0</td>
<td>0.263(18)</td>
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Table 5. Anisotropic displacement parameters (Å²) for Mn(NC NH₂)₄Cl₂ with standard deviations in parentheses.

<table>
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<tr>
<th>Atom</th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₂₃</th>
<th>U₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
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<td>0.0787(7)</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0059(4)</td>
<td>0.0854(8)</td>
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</tr>
<tr>
<td>N1</td>
<td>0.0590(9)</td>
<td>0.122(3)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>0.0528(9)</td>
<td>0.103(2)</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>N2</td>
<td>0.0578(11)</td>
<td>0.157(12)</td>
<td>0</td>
<td>0.0062(18)</td>
<td>0.0055(14)</td>
</tr>
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Table 6. Crystallographic data for Cr(NC NH₂)₄Cl₂.

<table>
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<th>Wyckoff position</th>
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<th>y</th>
<th>z</th>
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<tbody>
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<td>0</td>
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<td>0</td>
<td>0.053(2)</td>
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<tr>
<td>Cl</td>
<td>12e</td>
<td>0</td>
<td>0</td>
<td>0.2829(3)</td>
<td>0</td>
<td>0.044(2)</td>
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<tr>
<td>N1</td>
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<td>0</td>
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<td>0</td>
<td>0.064(5)</td>
</tr>
<tr>
<td>C</td>
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<td>0</td>
<td>0.049(7)</td>
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<td>N2</td>
<td>4kg</td>
<td>0.2511(5)</td>
<td>0.029(2)</td>
<td>0.2511(5)</td>
<td>0</td>
<td>0.059(10)</td>
</tr>
</tbody>
</table>

Table 7. Positional and isotropic displacement parameters (Å²) for Cr(NC NH₂)₄Cl₂ with standard deviations in parentheses.

Magnetic measurements

The temperature-dependent magnetic susceptibilities of 1 and 2 were determined by SQUID magnetometry (Quantum Design MPMS 5XL) between 2 and 300 K in applied fields of 0.1, 0.5 and 1.0 Tesla. The corresponding data of 3 and 4 were taken from a previous publication [2]. All data were corrected for the sample holder (PTFE capsules), and for diamagnetic contributions of the metal ions (Cr²⁺, Mn²⁺, Co³⁺, and Ni²⁺) and the ligands, calculated from tabulated values; χ_m = −119 × 10⁻¹¹ m³ mol⁻¹ K⁻¹ [22, 23].

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