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The Crystal and Molecular Structures of Twinned $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$: A New Complex Bimetallic Compound

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The complex bimetallic salt $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$ crystallizes in the space group $Fd\bar{3}$ with $a = 20.440(2)$ Å and $Z = 16$. The crystal and molecular structures have been determined from single crystal data, despite a systematic twinning ($R_F = 0.037$, $R_I = 0.041$ for 1065 reflections). The spatial arrangement consists in discrete $[Cr(NH_3)_6]^{3+}$, $[Ni(H_2O)_6]^{2+}$, Cl^-, and NH_4^+ ions, held together by ionic forces and by a network of hydrogen bonds. Both chromium and nickel ions are in octahedral sites. Structural correlations with related compounds are examined.

Introduction

We have recently been interested in the magnetic and structural properties of complex bimetallic compounds. Thus, we have reported on the magnetostructural properties of compounds such as $[Co(NH_3)_6][CuCl_5]$ (*1*), $[Co(NH_3)_6][FeCl_6]$ (*2*), or $[Cr(en)_3][ZnCl_4]Cl$ (*3*). From a structural point of view these systems form rather symmetric unit cells, since in general both counterions have comparable size and a high symmetry. Consequently, when magnetic interactions are present, these compounds are good 3-D magnetic models below the ordering temperature, T_c. We are systematically studying the type and magnitude of the interactions present in such systems by changing the magnetic ion or the ligands. When the magnetic moment of the counterions differ in either magnitude or anisotropy, ferrimagnetism may appear below T_c. Thus, we have recently reported the magnetic properties of the bimetallic salts $[Cr(H_2O)(NH_3)_5][FeCl_6]$, $[Cr(H_2O)_2(NH_3)_4][FeCl_6]$, and $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$ (*4*). These three compounds exhibit ferrimagnetic behavior below a critical temperature.

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The spin states of chromium and iron ions are, respectively, $S = 3/2$ and $S = 5/2$.

In this context the bimetallic salt $[Cr(NH_3)_6]NiCl_5$ was thought to be an interesting choice to study the influence of changing the magnetic ion, since the spin of the Ni^{2+} in this compound is $S = 1$. However, only crystals of $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$ could be isolated. This feature is rather common in the process of growing crystals of complex bimetallic salts and it is caused by the competition between kinetics and thermodynamic equilibriums. As an example, in the process of growing crystals of $[Cr(en)_3][FeCl_6]$ we have obtained $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$ or $[Cr(en)_3][FeCl_4]Cl_2 \cdot 9H_2O$ (*5*); however, when powder samples are prepared they present the desired stoichiometry. The same behavior is found in $[Co(en)_3][FeCl_6]$ (isolated as powder sample) and $[Co(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$ (isolated as single crystal) (*5*).

We report here the molecular and crystal structures of the new complex bimetallic salt $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$. Structural correlations with related compounds are also examined.

TABLE I

CRYSTAL DATA AND CONDITIONS OF DATA COLLECTION AND REFINEMENT FOR $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$

Temperature	293 K
Symmetry	Cubic
Space group	$Fd\bar{3}$
Cell parameters	$a = 20.440(2)$ Å $V = 8539.7$ Å^3; $Z = 16$
Crystal volume	1.41×10^{-2} mm^3
Radiation	Mo$K\alpha$ (graphite monochromatized)
Scanning mode	$\omega/2\theta$
Range registered	
θ_{min}, θ_{max}	1.7°, 45.0°
h,k,l max	40, 40, 40
Absorption correction	Gaussian method
Absorption coefficient μ (cm^{-1})	20.39
Transmission factors	Max : 0.6611 Min : 0.6284
Reflections measured	
Total	3552
Independent ($R_{average}$)	2156 ($R_{av} = 0.018$)
Used in refinement	1065 ($I_0 > 3\sigma(I_0)$)
Number of refined parameters	48 (with anisotropic thermal parameters)
Reliability factors	$R_F = (\Sigma \mid \lvert F_0 \rvert - k \lvert F_c \rvert \mid / \Sigma \mid F_0 \mid) = 0.037$ $R_I = (\Sigma \mid I_0 - kI_c \mid / I_0) = 0.041$

Experimental

Orange crystals of $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$ can be grown by mixing $[Cr(NH_3)_6](NO_3)_3$ and $NiCl_2 \cdot 6H_2O$ (1 : 5) in 2.5 *N* HCl. The solution is left to evaporate very slowly in a dessicator over a drying agent. Octahedral crystals as large as $3 \times 3 \times 3$ mm^3 were obtained by this method. The sample was chemically identified by elemental analysis. Calculated: Cr, 9.90; Ni, 11.18; Cl, 37.19; N, 17.33; H, 6.09. Found: Cr, 9.87; Ni, 11.20; Cl, 37.05; N, 17.60; H, 6.10.

A small crystal with an approximate volume of 1.41×10^{-2} mm^3 and octahedral shape was selected for the crystallographic determination. The data were collected on a Siemens AED2 four-circle diffractometer. The lattice parameter, $a = 20.440(2)$ Å, was refined from 48 reflections by a double-scan technique. The conditions of the diffraction experiment are summarized in Table I.

Data Analysis

The Laue symmetry $m3$ and the observed reflection conditions lead unambiguously to the space group $Fd\bar{3}$. Intensities, corrected for Lorentz polarization effects as well as for absorption using the correct final composition, were averaged in Laue group $m3$ and led to an R_{av} value of 0.018.

In the first trial, the structure was solved by direct methods (option EEES of the SHELX76 program (*6*)). Atomic scattering factors and anomalous dispersion parameters were taken from "International Tables for X-ray Crystallography" (*7*). The refinement with all non-hydrogen atoms converged to $R = 0.135$ and $R = 0.078$ for isotropic and anisotropic thermal motions, respectively (17 and 32 refined parameters for 1065 reflections). At this stage, a clear peak on the Fourier difference map indicated a possibility of disorder in the oxygen coordination sphere of nickel ion. Taking into account a certain degree of disorder, a residual $R = 0.064$ was obtained. The disorder was 26.3(9)% on two oxygen sites curiously related by a y,x,z symmetry operator. In addition, only two hydrogens of each NH_3 group could be clearly located. The third hydrogen appears distributed between two sites related by the same symmetry operator. The remaining hydrogens were not located.

Since the intensity ratio of the *hkl* and *khl* reflections was never greater than 2.4, the possibility that there could be no disorder but a twinning effect was considered. The superposition of the *hkl* and *khl* reflections from two crystallographic domains could lead to an apparent *m*3*m* Laue symmetry when the volume ratio of the domains is equal to 1. When the volume ratio is different to 1, an apparent partial disorder would be observed between sites related by a y,x,z symmetry operator. Such a hypothesis would be justified if clear improvement of the residuals arises.

To carry out a structural refinement within space group *Fd*3, we have minimized the function $\tau^2 = \Sigma\ \omega_i(I_0 - I_c)^2$, with $I_c = k_1\ |F_{hkl}|^2 + k_2|F_{khl}|^2$, where k_1 and k_2 stand for the scale factors of the two domains and $\omega_i = 1/I_0$ for the weighting scheme. This method has already been successfully applied to the resolution of some other complicated structures (*8, 9*). Taking into account the twinning hypothesis, the refinement with all non-hydrogen atoms converged to $R_F = 0.042$, corresponding to a volume ratio of the two domains equal to 2.16(1). When all the measured intensities originate from the superposition of two reflections, the only way to obtain the domains volume ratio is considering both contributions in the refinement. This reduces the degree of significance of a Fourier difference made from the mathematically untwinned data. In fact, five of the six hydrogen sites were suggested in the Fourier map; however, their coordinates could not be refined unless the NH_3 and H_2O ligands were restrained to rigid geometries. The final reliability factor drop to $R_F = 0.037$ (48 parameters, 1065 reflections). This result supports the twinning hypothesis well.

The positional and thermal motion parameters are listed in Table II. A table of I_0 and I_c can be obtained on request to the authors.

Description of the Structure and Structural Correlations

The crystal structure contains discrete $[Cr(NH_3)_6]^{3+}$, $[Ni(H_2O)_6]^{2+}$, Cl^- and NH_4^+ ions, held together by ionic forces and by a network of hydrogen bonds. The main interatomic distances and angles are listed in Table III. The arrangement of the octahedra in the unit cell is illustrated in Fig. 1. All the Cr–N bonds are symmetrically equivalent, as are the Ni–O bonds. The Cr–N bond distance is 2.071(2) Å, in excellent agreement with the values of 2.071(3), 2.073(2), and 2.071(3) Å found in, respectively, $[Cr(NH_3)_6][ZnCl_4]Cl$ (*10*), $[Cr(NH_3)_6][FeF_6]$ (*11*), and $[Cr(NH_3)_6][MnCl_5(H_2O)]$ (*12*). They also agree with those observed in other complex bimetallic salts containing Cr–N bonds (*11, 13*). The Ni–O distance of 2.040(3) Å in $[Ni(H_2O)_6]^{2+}$ is about the same as that of 2.048 and 2.050(8) Å in $Ni(OCOCH_3)_2 \cdot 4H_2O$ (*14*) and $Ni(NH_4)_2P_4O_{12} \cdot 7H_2O$ (*15*), respectively. The $[Cr(NH_3)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$ coordination polyhedra are very close to octahedral with no angular deviation from this symmetry greater than

TABLE II

ATOMIC PARAMETERS (10^4), ANISOTROPIC TEMPERATURE FACTORS[a] $U_{ij} \times 10^4$, AND B_{eq} ($Å^2$) FOR $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$[b]

Atom	Site	x	y	z	B_{eq} ($Å^2$)
Cr	16*d*	1/2	1/2	1/2	2.04(1)
Ni	16*c*	0	0	0	3.11(2)
Cl(1)	32*e*	2277(1)	2277(1)	2277(1)	4.90(3)
Cl(2)	48*f*	3983(0)	1/8	1/8	3.42(2)
Cl(3)	8*b*	5/8	5/8	5/8	3.85(5)
N(1)	96*g*	3987(1)	2495(2)	2493(2)	3.89(25)
N(2)	8*a*	1/8	1/8	1/8	6.69(30)
O	96*g*	867(1)	2769(2)	2085(2)	5.90(16)
H(1)	96*g*	3803(15)	2947(8)	2549(13)	4.74
H(2)	96*g*	3801(15)	2223(11)	2862(10)	4.74
H(3)	96*g*	3786(15)	2317(12)	2083(10)	4.74
H(4)	96*g*	900(18)	3183(13)	1836(18)	7.90
H(5)	96*g*	1324(11)	2594(17)	2150(20)	7.90
H(6)	32*e*	1534(5)	1534(5)	1534(5)	7.90

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr	258(1)	258(1)	258(1)	5(2)	5(2)	5(2)
Ni	394(2)	394(2)	394(2)	120(2)	120(2)	120(2)
Cl(1)	620(4)	620(4)	620(4)	139(4)	139(4)	139(4)
Cl(2)	362(4)	469(3)	469(3)	−48(4)	0(0)	0(0)
N(1)	302(9)	621(46)	554(43)	146(11)	−13(17)	7(17)
O	465(14)	850(22)	924(24)	479(17)	−63(15)	−128(14)

Note. Numbers in parentheses indicate esd's.

[a] The vibrational coefficients relate to the expression: $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2klb^*c^*U_{23})]$.

[b] $[Cr(NH(1)H(2)H(3))_6][Ni(H(4)H(5)O)_6]Cl(1)_2Cl(2)_3 \cdot 1/2[N(2)H(6)_4Cl(3)]$.

0.7 and 0.9°, respectively. Highly symmetrical octahedra are also found in other bimetallic salts such as $[Co(NH_3)_6][FeCl_6]$ (*16*), $[Co(NH_3)_6][TlCl_6]$ (*17*), $[Co(NH_3)_6][TlBr_6]$ (*17*), $[Co(NH_3)_6][Co(CN)_6]$ (*18*), $[Cr(NH_3)_6][MnF_6]$ (*11*), or $[Cr(NH_3)_6][FeF_6]$ (*11*).

The arrangement of both $[Cr(NH_3)_6]^{3+}$ and $[Ni(H_2O)_6{}^{2+}$ polyhedra in the unit cell is compared to that found for the $[Cr(NH_3)_6]^{3+}$ octahedra in $[Cr(NH_3)_6][CuCl_5]$ (*19*), as illustrated in Figs. 2 and 3. It can be described by stacks of alternate $[Cr(NH_3)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$ polyhedra along the three crystallographic axes as found in $[Co(NH_3)_6][FeCl_6]$ (*16*) (Fig. 4). Another description of the spatial distribution of the octahedra consists of alternate *A*, *B* layers perpendicular to any of the three crystallographic axes. Each layer is formed by rows of octahedra aligned parallel to the [110], [101], and [011] crystallographic directions. The layers of type *A* consist of alternated rows of $[Cr(NH_3)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$ octahedra, while layers of *B* type are formed by rows where $[Cr(NH_3)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$ polyhedra run alternated. Rather similar arrangement can be found in other bimetallic salts; however, in $[Cr(NH_3)_6][CuCl_5]$ (*19*) only one type of octahedron ($[Cr(NH_3)_6]^{3+}$) is present (Fig. 3), while $[Co(NH_3)_6][FeCl_6]$ (*16*) consists of layers of type *A* only (Fig. 4). Finally, the Cl^- and NH_4^+ ions are located in the interstices left by the octahedra as shown in Fig. 5.

TABLE III

MAIN BOND DISTANCES (Å) AND ANGLES (°) FOR $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$

Cr–N(1)	6 × 2.071(2)	Ni–O	6 × 2.040(3)
N(1)–Cr–N(1)	180.0	O–Ni–O	180.0
	90.70(7)		89.1(1)
	89.29(7)		90.9(1)

Hydrogen bonding[a]

O–H(4) ··· O	84(2)	O ··· O	2.907(5)	H(4) ··· O	2.83(4)
O–H(5) ··· O	73(2)	O ··· O	2.863(6)	H(5) ··· O	2.98(3)
N(1)–H(3) ··· N(1)	87(2)	N(1) ··· N(1)	2.911(5)	H(3) ··· N(1)	2.78(3)
N(1)–H(1) ··· N(1)	92(2)	N(1) ··· N(1)	2.946(5)	H(1) ··· N(1)	2.72(3)
O–H(5) ··· Cl(1)	177(3)	O ··· Cl(1)	3.078(3)	H(5) ··· Cl(1)	2.07(2)
O–H(4) ··· Cl(2)	164(3)	O ··· Cl(2)	3.112(4)	H(4) ··· Cl(2)	2.15(3)
N(1)–H(1) ··· Cl(2)	118(2)	N(1) ··· Cl(2)	3.328(4)	H(1) ··· Cl(2)	2.73(2)
N(1)–H(3) ··· Cl(1)	108(2)	N(1) ··· Cl(1)	3.551(3)	H(3) ··· Cl(1)	3.11(3)

[a] The N–H, O–H, and H–H distances were constrained to 1.00(2), 1.00(2), and 1.63(3) Å, respectively. See text.

A three-dimensional network of hydrogen bonds holds the $[Cr(NH_3)_6]^{3+}$, $[Ni(H_2O)_6]^{2+}$, Cl^-, and NH_4^+ ions together (Table III). An H_2O group forms two hydrogen bonds to Cl(1) and Cl(2) atoms with O ··· Cl distances of 3.078(3) and 3.112(4) Å, respectively. The amine ligands are also connected to Cl(2) and Cl(1) atoms with N(1)···Cl distances of 3.328(4) and 3.551(3) Å. O — H ··· O and N(1) — H ··· N(1) hydrogen bonds are also

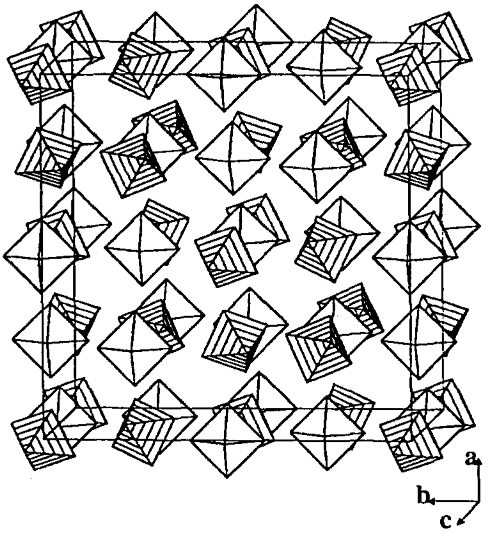

FIG. 1. Arrangement of the $[Cr(NH_3)_6]^{3+}$ (unhatched) and $[Ni(H_2O)_6]^{2+}$ (hatched) octahedra in $[Cr(NH_3)_6][Ni(H_2O)_6Cl_5 \cdot 1/2(NH_4Cl)$. All the figures were executed with STRUPLO (*20*).

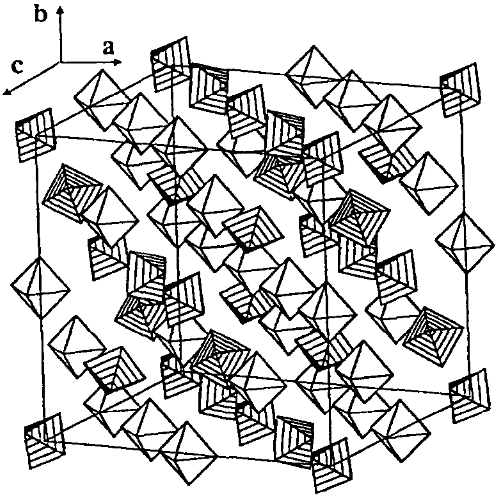

FIG. 2. Stacks and layers of $[Cr(NH_3)_6]^{3+}$ (unhatched and $[Ni(H_2O)_6{}^{2+}$ (hatched) octahedra in $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$.

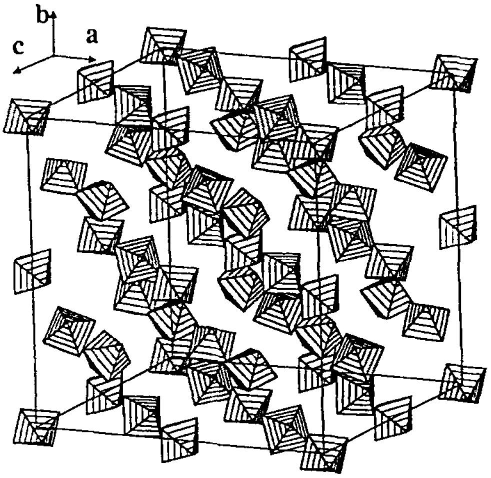

FIG. 3. Spatial distribution of octahedra in $[Cr(NH_3)_6][CuCl_5]$, to be compared with that found in $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$.

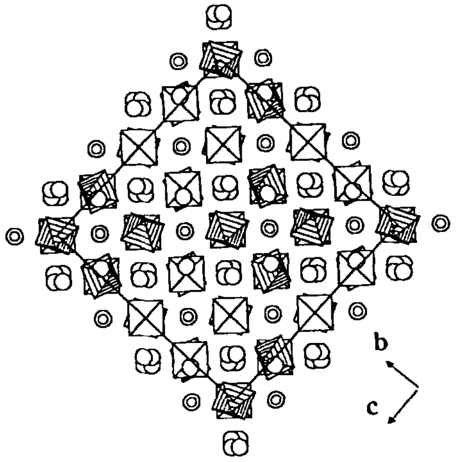

FIG. 5. Projection of the structure of $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$ on the (100) plane. Octahedra stand for $[Cr(NH_3)_6]^{3+}$ (unhatched) and $[Ni(H_2O)_6]^{2+}$ (hatched). Large circles represent the Cl^- anions while small ones stand for the NH_4^+ cations.

present. On the other hand, the complex cations and anions are not directly linked by hydrogen bonds as found in other bimetallic salts such as $[Cr(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$ (5); there are no N(1) ··· O contacts in the structure of $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$, probably due to the interstitial location of isolated Cl^- and NH_4^+ ions which separate the $[Cr(NH_3)_6]^{3+}$ and $[Ni(H_2O)_6]^{2+}$ ions enough to prevent formation of hydrogen bonds. The value of the distance between the NH_4^+ group and the chlorine atom Cl(1) is 3.636(1) Å which may be interpreted as an incipient formation of an hydrogen bond. In a similar way could be explained the contact between the Cl(3) atom and the NH_3 group, with a distance of 3.664(2) Å.

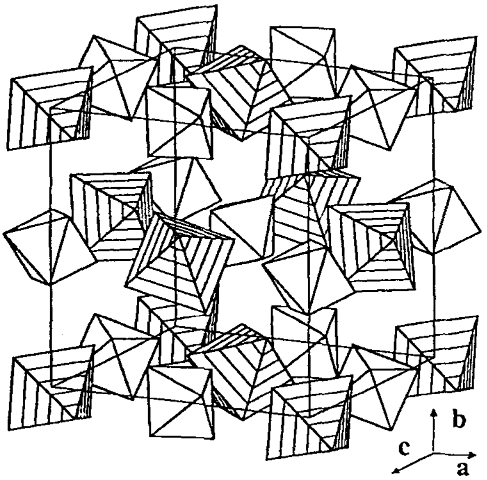

FIG. 4. Stacks and layers of $[Co(NH_3)_6]^{3+}$ (unhatched) and $[FeCl_6]^{3-}$ (hatched) octahedra in $[Co(NH_3)_6][FeCl_6]$, to be compared with those found in $[Cr(NH_3)_6][Ni(H_2O)_6]Cl_5 \cdot 1/2(NH_4Cl)$.

Such a symmetric structure should lead, below an ordering temperature T_c, to a good model system of 3-D magnetic ordering since expected magnetic superexchange pathways are very symmetric as well. Alternating current magnetic susceptibility measurements are in progress.

Acknowledgments

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