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Crystal Structure and Magnetic Measurements of $[Cr(en)_3][ZnCl_4]Cl$

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Abstract

The compound $[Cr(en)_3][ZnCl_4]Cl$ has been synthesized by reaction of $CrCl_3 \cdot 6H_2O$, Zn and $[Cr(en)_3]_2(SO_4)_3$ in HCl. Its molecular and crystalline structure was determined by X-ray diffraction methods, being monoclinic, $P2_1/c$, $a = 21.215(3)$, $b = 12.532(2)$, $c = 13.707(2)$ Å, $\beta = 95.21°$, $V = 3629(2)$ Å^3, $D_x = 1.738$ g cm^{-3}, $MW = 474.9$, $Z = 8$, $F(000) = 1928$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 27.04 cm^{-1}, 288 K. No significant exchange interactions between Cr(III) cations in the crystalline lattice were found. Curie–Weiss behavior was found in the three directions tested ($g_1 = 2.06 \pm 0.02$, $g_2 = 2.08 \pm 0.02$, $g_3 = 2.09 \pm 0.01$), $T = 1.2$–1.4 K.

Introduction

As a part of our research program in magnetochemistry, we have synthesized several families of double complex salts and studied their magnetic behaviour [1]. In this way we have prepared several $[CrCl_6]^{3-}$ salts with different amines or amine complexes like $[M(NH_3)_6]^{3+}$ or $[M(en)_3]^{3+}$ as counter ion [2]. The synthesis starts from $CrCl_3$ in HCl using powdered metallic Zn as catalyst as is usual in Cr(III) chemistry. In an attempt to grow single crystals for X-ray characterization and magnetic susceptibility measurements of these hexachloro chromate(III) complexes we have found instead excellent large crystals of $[Cr(en)_3][ZnCl_4]Cl$.

Few examples are known of halozincate complexes well documented by X-ray diffraction methods. To our knowledge all these halozincate complexes are tetrachlorozincate(II) of complexes cations, this is true such as recently reported [3] in $[Co(C_5H_5NO)_6][ZnCl_4]$, in spite of the efforts of several authors to synthesize penta and hexachloro zincates(II).

Using the trivalent complex cations $[Co(NH_3)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$, the compounds $[Co(NH_3)_6]$-$[ZnCl_4]Cl$ [4] and $[Cr(NH_3)_6][ZnCl_4]Cl$ [5] were reported. Surprisingly these compounds are not isomorphous, belonging to the orthorhombic, *Pnma* and trigonal, $R\bar{3}c$ space groups, respectively. The author observed disorder in the $[ZnCl_4]^{2-}$ and Cl^- anions in the last structure.

On the other hand, using the divalent amine-complex cation β-chloro(ethylenediamine)(dipropylenetriamine)cobalt(III), the simpler tetrachloro zincate(II), β-[Co(en)(dpt)Cl][$ZnCl_4$] [6] was synthesized, space group monoclinic $P2_1/c$.

All these facts suggested to us that, despite the stoichiometry presence of five chloride ions per zinc ion, tetracoordination is more favoured than penta or higher coordination in these anionic Zn(II) complexes; the more or less simple compound stoichiometry apparently depends on the charge of the cation.

In this paper we report a complete study of the characterization by X-ray diffraction methods and magnetic susceptibility measurements on a single crystal of the compound $[Cr(en)_3][ZnCl_4]Cl$.

Experimental

Synthesis of [Cr(en)$_3$][ZnCl$_4$]Cl

To a solution of $CrCl_3 \cdot 6H_2O$ (4.0 g, 0.015 mol) in hot and concentrated HCl (10 ml), powdered metallic Zn (0.1 g) was added. The mixture was left to stand

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for a few minutes, while an intense release of H_2 gas was observed. To the aforementioned solution, solid $[Cr(en)_3]_2(SO_4)_3$ [7] (1.5 g, 0.0028 mol) was added. After 30 min an orange solid began to precipitate, which was filtered. Chemical analyses and spectrophotometric evidence suggested that the powder collected is $[Cr(en)_3][CrCl_6]$. Crystals of another compound, suitable for X-ray diffraction, were collected from the mother liquor after one month in the dark. X-ray diffraction analyses gave us the evidence the crystals were $[Cr(en)_3][ZnCl_4]Cl$. Found: C, 15.74; H, 4.97; N, 17.44; Cl, 37.09; Cr, 10.81. Calc. for $[Cr(en)_3][ZnCl_4]Cl$: C, 15.16; H, 5.05; N, 17.69; Cl, 37.38; Cr, 10.95%.

X-ray Data Collection and Reduction

Crystal data: $MW = 474.9$, monoclinic, $P2_1/c$, $a = 21.215(3)$, $b = 12.532(2)$, $c = 13.707(2)$ Å, $\beta = 95.21°$, $V = 3629(2)$ Å^3, $D_x = 1.738$ g cm^{-3}, $Z = 8$, $F(000) = 1928$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 27.04 cm^{-1}, 288 K.

A prismatic crystal 0.15 × 0.15 × 0.2 mm) was selected and mounted on a Phillips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from 25 reflections ($4° < \theta < 12°$) and refined by least-squares. Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω-scan technique, scan width 0.8°, scan speed 0.03 s^{-1}. 5434 reflections were measured in the range $2° < \theta < 25°$; 5000 of which were assumed as observed applying the condition $I > 2.5\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control, significant intensity decay was not observed. Lorentz polarization and absorption corrections were made.

The Zn and Cr atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms from a weighted Fourier synthesis. The structure was refined by the least-squares method using the SHELX76 computer program [8]. The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.0022|F_o|^2]^{-1}$. The final R was 0.032 (R_w = 0.035) for all observed reflections. The scattering factors were taken from the International Tables for X-ray Crystallography [9].

Spectral and Magnetic Susceptibility Measurements

Electronic spectra were measured on a Shimadzu 240 Vis–UV spectrophotometer in aqueous solution. IR spectra were recorded on a Beckman IR-20 spectrophotometer as KBr pellets. Susceptibility measurements were made as described previously [1a, 1b] by an ac method.

Results and Discussion

The electronic spectra in aqueous solution show two bands in the visible region at 458 nm (ϵ = 76.1 mol^{-1} cm^2) and 350 nm (ϵ = 60.5 mol^{-1} cm^2) which are typical for the $[Cr(en)_3]^{3+}$ cation [10]. IR spectra show the expected bands attributable to the ethylenediamine ligand.

Description of the Structure

The structure consists of octahedral $[Cr(en)_3]^{3+}$ cations, tetrahedral $[ZnCl_4]^{2-}$ anions and Cl^- ions, linked by van der Waals, ionic forces and hydrogen bonds. There are two non-equivalent ion pairs: $[Cr(en)_3]^{3+}$, $[ZnCl_4]^{2-}$ in the unit cell, giving eight $[Cr(en)_3][ZnCl_4]Cl$ units related by symmetry operations. Figure 1 shows the packing of the ions in the unit cell, and Fig. 2 shows the local environment of the zinc ion. Final atomic coordinates are given in Table I. Tables II and III show the interionic bond lengths and bond angles, respectively, of the cation and anion.

The two non-equivalent Zn(II) ions display a distorted tetrahedral coordination with a Cl–Zn

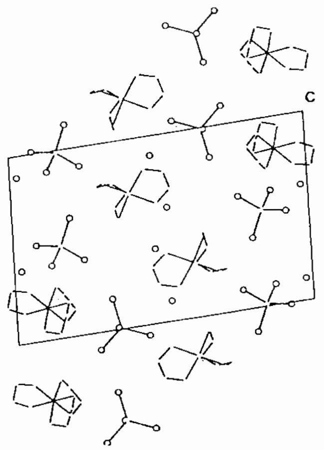

Fig. 1. The packing of the ions in $[Cr(en)_3][ZnCl_4]Cl$ viewed along the b axis (projection on the ac plane).

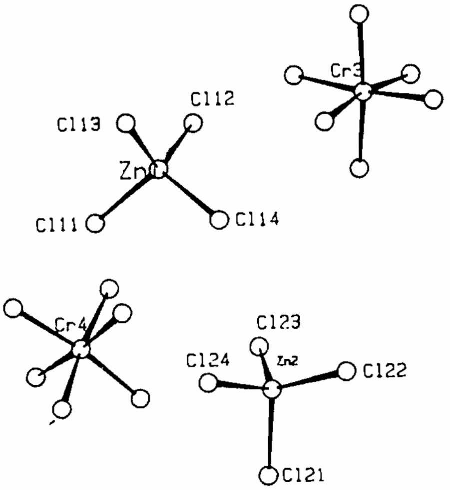

Fig. 2. The local environment of the zinc ion.

TABLE I. Final Atomic Coordinates (x 10^4) of [Cr(en)$_3$]-[ZnCl$_4$]Cl

	x/a	*y/b*	*z/c*	B_{eq}
Zn(1)	15885(2)	3255(3)	1275(3)	3.10(2)
Zn(2)	34776(2)	−44139(3)	99244(3)	3.37(2)
Cl(11)	7801(3)	−8879(5)	−1004(7)	3.57(4)
Cl(12)	19452(4)	8943(7)	−12775(8)	4.18(4)
Cl(13)	12623(4)	16274(6)	10948(8)	4.65(5)
Cl(14)	23657(4)	−5579(9)	10416(8)	4.92(5)
Cl(21)	34062(4)	37138(6)	99049(7)	3.87(4)
Cl(22)	44339(4)	61255(6)	5819(7)	3.87(4)
Cl(23)	32416(4)	−39528(7)	83703(7)	4.22(4)
Cl(24)	27609(4)	−39448(7)	109610(8)	4.47(4)
Cl(1)	97618(4)	14995(6)	38345(8)	4.34(4)
Cl(2)	52335(4)	−36716(5)	39503(6)	3.48(3)
Cr(3)	39934(2)	12290(3)	−20711(4)	2.29(2)
Cr(4)	10577(2)	−39368(3)	83022(4)	2.34(2)
N(31)	3103(1)	1404(2)	−2823(2)	3.20(12)
C(31)	2876(2)	2484(3)	−2659(4)	5.03(17)
C(32)	3414(2)	3255(2)	−2746(3)	4.67(17)
N(32)	3968(1)	2891(2)	−2076(2)	3.54(12)
N(33)	4506(1)	1222(2)	−3278(2)	2.64(11)
C(33)	5174(1)	959(3)	−2984(3)	3.54(15)
C(34)	5372(1)	1515(3)	−2021(3)	3.44(14)
N(34)	4892(1)	1231(2)	−1335(2)	2.78(11)
N(35)	3910(1)	−445(2)	−2139(2)	2.90(11)
C(35)	3489(1)	−790(2)	−1408(3)	3.72(15)
C(36)	3629(2)	−152(3)	−502(3)	3.55(15)
N(36)	3583(1)	993(2)	−760(2)	3.05(11)
N(41)	443(1)	−4807(2)	7310(2)	3.11(11)
C(41)	−161(1)	−4178(2)	7097(3)	3.57(14)
C(42)	−309(1)	−3611(2)	8025(3)	3.44(14)
N(42)	251(1)	−2989(2)	8435(2)	3.59(11)
N(43)	1762(1)	−5059(2)	8184(2)	3.60(12)
C(43)	1649(2)	−6022(2)	8826(3)	4.24(16)
C(44)	1435(2)	−5614(2)	9773(3)	4.34(17)
N(44)	877(1)	−4875(2)	9489(2)	3.25(12)
N(45)	1629(1)	−2928(2)	−794(2)	3.43(11)
C(45)	1988(2)	−2190(3)	8607(3)	5.06(18)
C(46)	1601(1)	−1913(2)	7698(3)	4.00(16)
N(46)	1360(1)	−2984(2)	7206(2)	3.60(12)

bond length (2.351(3) or 2.292(3) Å) larger than the remaining Cl–Zn bonds (average 2.255(3) or 2.240(3) Å). The distortion of the tetrahedron should be due to the proximity of the Cl$^-$ ions suggesting a pseudo pentacoordination of these ions to the Zn atom.

The Cr(III) ion displays a distorted octahedral coordination with an average Cr–N bond length of 2.08(1) Å and an inner bond angle of 82.5(6)°.

The crystalline structure can be advantageously viewed by a projection on the ac plane, and described by layers of alternate [Cr(en)$_3$]$^{3+}$ cations and [ZnCl$_4$]$^{2-}$ anions, intercalated by layers of Cl$^-$ or vacant sites. Table IV shows the shortest van der Waals or assignable hydrogen bonds. No effective superexchange pathways are obvious in the crystal structure.

TABLE II. Bond Lengths for [Cr(en)$_3$][ZnCl$_4$]Cl

Cl(11)–Zn(1)	2.292(1)
Cl(12)–Zn(1)	2.248(1)
Cl(13)–Zn(1)	2.251(1)
Cl(14)–Zn(1)	2.267(1)
Cl(21)–Zn(2)	2.351(1)
Cl(22)–Zn(2)	2.248(1)
Cl(23)–Zn(2)	2.220(1)
Cl(24)–Zn(2)	2.251(1)
N(31)–Cr(3)	2.080(2)
N(32)–Cr(3)	2.084(2)
N(33)–Cr(3)	2.061(2)
N(34)–Cr(3)	2.074(2)
N(35)–Cr(3)	2.107(2)
N(36)–Cr(3)	2.088(2)
N(41)–Cr(4)	2.101(2)
N(42)–Cr(4)	2.104(2)
N(43)–Cr(4)	2.068(2)
N(44)–Cr(4)	2.071(2)
N(45)–Cr(4)	2.080(2)
N(46)–Cr(4)	2.067(2)
C(31)–N(31)	1.462(4)
C(32)–C(31)	1.509(4)
N(32)–C(32)	1.494(4)
C(33)–N(33)	1.475(3)
C(34)–C(33)	1.518(4)
N(34)–C(34)	1.490(4)
C(35)–N(35)	1.467(4)
C(36)–C(35)	1.484(4)
N(36)–C(36)	1.479(3)
C(41)–N(41)	1.510(3)
C(42)–C(41)	1.514(4)
N(42)–C(42)	1.489(3)
C(43)–N(43)	1.525(3)
C(44)–C(43)	1.503(5)
N(44)–C(44)	1.525(3)
C(45)–N(45)	1.492(4)
C(46)–C(45)	1.471(5)
N(46)–C(46)	1.567(3)

Magnetic Measurements

Magnetic susceptibility measurements have been carried out on a 7.00 mg crystal with hexagonal habit from 4.2 down to 1.2 K. The measurements have been made on the crystal oriented along three perpendicular directions, one of them coincident with the pseudohexagonal axis. The magnetic measurements do not show significant interactions between paramagnetic centers.

The magnetic susceptibilities follow the Curie–Weiss law. The inverse of the magnetic susceptibility follows a straight line (correlation coefficient of the linear regression, 0.9999) with a temperature axis intercept of 0.265 ± 0.002, 0.066 ± 0.002 and 0.197 ± 0.002 K, respectively. These small Weiss temperatures could be explained by zero field splitting effects in the Cr(III) ions.

The Curie constants calculated from the slope of the straight line are 1.98, 2.03, 2.04 and the *g* param-

TABLE III. Bond Angles for $[Cr(en)_3][ZnCl_4]Cl$

Cl(12)–Zn(1)–Cl(11)	113.5( )
Cl(13)–Zn(1)–Cl(11)	107.2( )
Cl(13)–Zn(1)–Cl(12)	114.8( )
Cl(14)–Zn(1)–Cl(11)	104.4( )
Cl(14)–Zn(1)–Cl(12)	110.1( )
Cl(14)–Zn(1)–Cl(13)	106.0( )
Cl(22)–Zn(2)–Cl(21)	111.1( )
Cl(23)–Zn(2)–Cl(21)	103.9( )
Cl(23)–Zn(2)–Cl(22)	115.0( )
Cl(24)–Zn(2)–Cl(21)	102.8( )
Cl(24)–Zn(2)–Cl(22)	107.8( )
Cl(24)–Zn(2)–Cl(23)	115.5( )
N(32)–Cr(3)–N(31)	82.6(1)
N(33)–Cr(3)–N(31)	97.1(1)
N(33)–Cr(3)–N(32)	91.0(1)
N(34)–Cr(3)–N(31)	173.8(1)
N(34)–Cr(3)–N(32)	91.3(1)
N(34)–Cr(3)–N(33)	82.0(1)
N(35)–Cr(3)–N(31)	90.8(1)
N(35)–Cr(3)–N(32)	173.3(1)
N(35)–Cr(3)–N(33)	90.5(1)
N(35)–Cr(3)–N(34)	95.3(1)
N(36)–Cr(3)–N(31)	90.6(1)
N(36)–Cr(3)–N(32)	97.5(1)
N(36)–Cr(3)–N(33)	169.2(1)
N(36)–Cr(3)–N(34)	91.1(1)
N(36)–Cr(3)–N(35)	81.8(1)
N(42)–Cr(4)–N(41)	83.5(1)
N(43)–Cr(4)–N(41)	90.4(1)
N(43)–Cr(4)–N(42)	171.5(1)
N(44)–Cr(4)–N(41)	93.8(1)
N(44)–Cr(4)–N(42)	92.4(1)
N(44)–Cr(4)–N(43)	82.1(1)
N(45)–Cr(4)–N(41)	173.8(1)
N(45)–Cr(4)–N(42)	92.3(1)
N(45)–Cr(4)–N(43)	94.3(1)
N(45)–Cr(4)–N(44)	90.9(1)
N(46)–Cr(4)–N(41)	92.6(1)
N(46)–Cr(4)–N(42)	92.6(1)
N(46)–Cr(4)–N(43)	93.5(1)
N(46)–Cr(4)–N(44)	172.3(1)
N(46)–Cr(4)–N(45)	83.1(1)
C(31)–N(31)–Cr(3)	108.6(2)
C(32)–C(31)–N(31)	108.5(2)
N(32)–C(32)–C(31)	103.4(2)
C(32)–N(32)–Cr(3)	109.0(2)
C(33)–N(33)–Cr(3)	110.2(2)
C(34)–C(33)–N(33)	108.6(2)
N(34)–C(34)–C(33)	106.7(2)
C(34)–N(34)–Cr(3)	110.2(2)
C(35)–N(35)–Cr(3)	108.5(2)
C(36)–C(35)–N(35)	109.0(2)
N(36)–C(36)–C(35)	108.6(2)
C(36)–N(36)–Cr(3)	108.6(2)
C(41)–N(41)–Cr(4)	108.7(2)
C(42)–C(41)–N(41)	108.7(2)
N(42)–C(42)–C(41)	110.0(2)
C(42)–N(42)–Cr(4)	107.4(2)
C(43)–N(43)–Cr(4)	109.9(2)
C(44)–C(43)–N(43)	107.7(2)
N(44)–C(44)–C(43)	106.0(3)
C(44)–N(44)–Cr(4)	110.5(2)
C(45)–N(45)–Cr(4)	110.4(2)
C(46)–C(45)–N(45)	109.8(2)
N(46)–C(46)–C(45)	107.4(2)
C(46)–N(46)–Cr(4)	107.0(2)

TABLE IV. Selected Interatomic Bond Lengths for $[Cr(en)_3][ZnCl_4]Cl$ [a]

Cl(14)(i)···Cl(23)	3.597(1)
Cl(21)(ii)···N(32)	3.231(2)
Cl(21)(iii)···N(31)	3.240(2)
Cl(21)(iii)···N(33)	3.256(2)
Cl(1)(iv)···N(46)	3.247(2)
Cl(1)(v)···N(44)	3.263(2)
Cl(2)(vi)···N(33)	3.267(2)
Cl(2)(vii)···N(35)	3.252(2)

[a] Symmetry code: (i) = $x, \frac{1}{2} - y, z + \frac{3}{2}$; (ii) = $x, y, z - 1$; (iii) = $x, \frac{3}{2} - y, z + \frac{3}{2}$; (iv) = $1 - x, -y, 1 - z$; (v) = $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (vi) = $1 - x, -y, -z$; (vii) = $x, \frac{1}{2} - y, z + \frac{1}{2}$.

eters calculated from the Curie constants assuming a spin value of 3/2 are 2.06 ± 0.02, 2.08 ± 0.02 and 2.09 ± 0.01, respectively. These values are typical for paramagnetic compounds containing magnetically diluted Cr(III) ions [11].

The absence of significant exchange interactions in this compound can be explained by the presence of the voluminous cation. The metal is well hidden in these chelates and there is no strong hydrogen bonding in the structure, nor are there short super-exchange pathways through the diamagnetic anions. Therefore one does not expect to find a very strong magnetic interaction. The behavior is similar to other ethylenediamine containing double salts studied by us [1b].

Supplementary Material

Tables of structure factors and anisotropic thermal parameters are available from the authors on request.

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References

1 (a) R. L. Carlin, R. Burriel, J. Pons and J. Casabó, *Inorg. Chem., 21,* 2905 (1982); (b) R. L. Carlin, R. Burriel, J. Pons and J. Casabó, *Inorg. Chem., 22,* 2832 (1983); (c) R. Burriel, J. Casabó, J. Pons, D. W. Carnegie and R. L. Carlin, *Physica B, 123,* 185 (1985); (d) J. Bartolomé, F. Lázaro, R. Burriel, J. Pons, J. Casabó and P. R. Nugteren, *J. Magn. Magn. Mater., 54–57,* 1503 (1986); (e) J. Casabó, T. Flor, F. Teixidor and J. Ribas, *Inorg. Chem., 25,* 3166 (1986); (f) T. Flor and J. Casabó, *Polyhedron, 6,* 1563 (1987).

2 J. Pons, *Doctoral Thesis,* Universitat Autónoma de Barcelona, 1986.

3 G. Menenga, L. G. deJongh, W. J. Huiskamp, E. Sinn, A. Lambrecht, R. Burriel and R. L. Carlin, *J. Magn. Magn. Mater., 44,* 77 (1984).

4 D. W. Meek and J. A. Ibers, *Inorg. Chem., 9,* 465 (1970).

5 W. Clegg, *Acta Crystallogr., Sect. B, 32,* 2907 (1976).

6 P. R. Ireland, D. A. House and W. T. Robinson, *Inorg. Chim. Acta, 4,* 137 (1970).

7 C. L. Rollison and J. C. Bailar Jr., *Inorg. Synth., 2,* 198 (1946).

8 G. M. Sheldrick, 'Shelx76', program for crystal structure determination, University of Cambridge, U.K., 1976.

9 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1974, pp. 99, 149. (Present distributor D. Reidel, Dordrecht.)

10 R. A. D. Wentworth and T. S. Piper, *Inorg. Chem., 4,* 709 (1965).

11 R. L. Carlin, 'Magnetochemistry', Springer-Verlag, New York, 1986, Chap. 4.