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Isostructuralism in Double Complex Salts Series: $[M(H_2O)_x(NH_3)_{6-x}][M'(CN)_6]$ and $[M(H_2O)_x(NH_3)_{6-x}][CuCl_5]$ (M, M′ = Co(III), Cr(III); x = 0, 1, 2). Crystal Structure of $[Cr(H_2O)(NH_3)_5][CuCl_5]$

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Abstract

Isostructuralism in two series of double complex salts $[M(H_2O)_x(NH_3)_{6-x}][M'(CN)_6]$ (M, M′ = Co(III), Cr(III); $x = 0$, 1, 2) and $[M(H_2O)_x(NH_3)_{6-x}][CuCl_5]$ (M = Co(III), Cr(III); $x = 0$, 1, 2) is reported by the use of X-ray powder diffraction methods. Compounds from the first series belong to the space group $R\bar{3}$, while those from the second belong to the $Fd3c$ group. The crystal structure of $[Cr(H_2O)(NH_3)_5][CuCl_5]$, solved by single crystal X-ray diffraction methods, is cubic, space group $Fd3c$, with $a = 22.208(3)$ Å, $V = 10952$ Å^3, $Z = 32$, $D_x = 1.92$ g cm^{-1}, $\mu = 9.57$ cm^{-1}, $F(000) = 6336$, $M_w = 395.98$. Disorder of the water molecule of the $[Cr(H_2O)(NH_3)_5]^{3+}$ cation among the six coordination sites of the octahedrally coordinated Cr(III) ion was found. A possible explanation of the isomorphism between the compounds within each series is proposed.

Introduction

Double salts containing complex cations and anions of the type $[Co(NH_3)_6][Co(CN)_6]$ are well known. Due to their generally low solubility they have been used to stabilize, by precipitation, species which are otherwise difficult to isolate [1].

The solid state thermal reactivity has been previously explored [2] as an approach to preparing μ-cyano dinuclear compounds of the type

$$[Co(H_2O)(NH_3)_5]\,[Co(CN)_6] \xrightarrow{\Delta} H_2O + [(NH_3)_5Co{-}NC{-}Co(CN)_5]$$

Recently there has been an increasing interest in these compounds because of their magnetic properties. They provide a new source of compounds exhibiting extended magnetic interactions which can be useful for testing theoretical models or they can originate new phenomena [3, 4]. The change of the metal and therefore of the spin, in the cationic or anionic units, is relatively easy in these bimetallic complex compounds and, on the other hand, their crystalline structures are normally simple and rather symmetric. For that reason they have proved to be excellent materials for 'crystal lattice architecture' in order to produce compounds with different magnetic properties [5].

Compounds of the two series here reported have been known for a long time, but they lack a systematic structural study. All the twelve compounds of general formula $[M(H_2O)_x(NH_3)_{6-x}][M'(CN)_6]$ (M, M′ = Co(III), Cr(III); $x = 0$, 1, 2) had been previously synthesized, with the exception of $[Co(H_2O)_2(NH_3)_4][Cr(CN)_6]$ and $[Cr(H_2O)_2(NH_3)_4][Cr(CN)_6]$. The crystal structures of $[Co(NH_3)_6][Cr(CN)_6]$ [6–8], $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$ [9] and $[Co(NH_3)_6][Co(CN)_6]$ (6, 7], have been reported. All of them are isomorphous belonging to the space group $R\bar{3}$. Figgis and Reynolds have pointed out the isostructuralism between some compounds of this series [10], but until now no systematic studies on the whole series have been undertaken.

In addition complex bimetallic salts of the type $[M(H_2O)_x(NH_3)_{6-x}][CuCl_5]$ (M = Co(III), Cr(III); $x = 0$, 1, 2) are studied in this paper with the exception of $[Cr(H_2O)_2(NH_3)_4][CuCl_5]$ which could not be synthesized. Some of them had already been reported in the literature (M = Co, $x = 0$ [11], $x = 1$ [12]; M = Cr, $x = 0$ [13]).

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The crystal structures of the compounds $[Co(NH_3)_6][CuCl_5]$ [14] and $[Cr(NH_3)_6][CuCl_5]$ [15] have been previously determined by X-ray diffraction methods. Both belong to the space group *Fd3c*. A number of papers devoted to elucidating the stereochemistry (TBP or SP) of the $[CuCl_5]^{3-}$ anion by spectrophotometric methods are found in the literature and several thermomagnetic studies on these compounds have been undertaken by different authors [16]. The behaviour of $[Cr(H_2O)(NH_3)_5][CuCl_5]$ and $[Co(NH_3)_6][CuCl_5]$ is worthy of mention. The first orders at 298 mK in a rather complicated way [5b], while the second has been described as one of the best known examples of the $S = \frac{1}{2}$, a simple cubic Heisenberg antiferromagnet model [17].

Experimental

Synthesis of the Bimetallic Complex Salts

Hexacyanometallate(III) series

Starting materials, $K_3[Co(CN)_6]$, $K_3[Cr(CN)_6]$, $[Co(NH_3)_6]Cl_3$, $[Cr(NH_3)_6](NO_3)_3$, $[Co(H_2O)(NH_3)_5]Cl_3$, $[Co(H_2O)(NH_3)_5](ClO_4)_3$, $[Cr(H_2O)(NH_3)_5](NO_3)_3$, *cis*-$[Co(H_2O)_2(NH_3)_4](ClO_4)_3$ and *cis*-$[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ were prepared as described in the literature.

The hexacyanocobaltate(III) complexes $[M(H_2O)_x(NH_3)_{6-x}][Co(CN)_6]$ (M = Co(III), Cr(III); $x = 0, 1, 2$) and the hexacyanochromate(III) complexes $[M(H_2O)_x(NH_3)_{6-x}][Cr(CN)_6]$ (M = Co(III), Cr(III); $x = 0, 1$) were synthesized. The compounds $[Co(H_2O)_2(NH_3)_4][Cr(CN)_6]$ and $[Cr(H_2O)_2(NH_3)_4][Cr(CN)_6]$ could not be isolated because of the formation of μ-CN species [18].

Stoichiometric amounts of the corresponding single complex salts were mixed to prepare the hexacyanometallate(III) of the ammine or aquaamminemetal(III) cations.

In a typical experiment, solid $K_3[Co(CN)_6]$ (2.49 g, 7.5 mmol) was added to a clear solution of $[Co(NH_3)_6]Cl_3$ (2 g, 7.5 mmol) in the minimum amount of water (25 ml). An orange solid began to precipitate (more or less quickly depending on the case) and acetic acid was added to complete the precipitation. The material was filtered, washed with ethanol (50 ml) and dried under vacuum. The compounds were stored in the dark.

Compounds *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ or *cis*-$[Cr(H_2O)_2(NH_3)_4][Co(CN)_6]$ were prepared by a different procedure. In a typical experiment an excess of solid $NaClO_4$ was added to a solution of $K_3[Co(CN)_6]$ (2.15 g) in water (5 ml). The insoluble $KClO_4$ was filtered and discarded. Then, a solution of *cis*-$[Co(H_2O)_2(NH_3)_4](ClO_4)_3$ (3 g) in water (5 ml) was mixed with the aforementioned clear solution and acetic acid was added to precipitate the *cis*-$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ compound. The solid was filtered, washed with ethanol, dried and stored as before.

All compounds analyzed correctly and their IR and electronic spectra were as expected.

Pentachlorocuprate(II) series

The following pentachlorocuprate(II) complexes were synthesized $[Co(NH_3)_6][CuCl_5]$, $[Cr(NH_3)_6][CuCl_5]$, $[Co(H_2O)(NH_3)_5][CuCl_5]$, $[Cr(H_2O)(NH_3)_5][CuCl_5]$ and *cis*-$[Co(H_2O)_2(NH_3)_4][CuCl_5]$.

In a typical experiment, to a solution of $[Co(NH_3)_6]Cl_3$ (2 g, 7.5 mmol) in the minimum amount of water (50 ml), solid $CuCl_2 \cdot 2H_2O$ (1.27 g, 7.5 mmol) was added. Then, concentrated HCl (20 ml) was mixed to the clear aforementioned solution and a yellow solid began to precipitate. The material was filtered, washed with ethanol (50 ml) and dried under vacuum. All compounds were stored in the dark. To obtain the compounds $[Co(H_2O)(NH_3)_5][CuCl_5]$ and *cis*-$[Co(H_2O)_2(NH_3)_4][CuCl_5]$, an excess of $CuCl_2 \cdot 2H_2O$ ($\simeq 10\%$) was added.

All compounds analyzed correctly and their IR and electronic spectra were as expected.

Elemental analyses were performed in our microanalytical laboratory on a Perkin-Elmer 240 B instrument. Electronic spectra were measured on a Beckman Acta-III or a Shimadzu UV-240 spectrophotometer in aqueous solution. IR spectral measurements were performed on a Beckman IR-20A spectrophotometer in KBr pellets.

X-ray Structure Determination

Single crystals of $[Cr(H_2O)(NH_3)_5][CuCl_5]$ are cubic, space group *Fd3c*, with $a = 22.208(3)$ Å, $V = 10952$ Å^3, $Z = 32$, $D_x = 1.92$ g cm^{-1}, $\mu = 9.57$ cm^{-1}, $F(000) = 6336$, $M_w = 395.98$.

X-ray diffraction data at 293 K were collected on a Syntex P2, four circle diffractometer using graphite crystal monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) on a $0.08 \times 0.08 \times 0.013$ mm yellow prismatic crystal. The cell parameters were calculated from ten reflections and refined by least-squares techniques. The number of independently collected reflections was 349 and 239 were considered as observed with $I > 2.5(\sigma)$. Three standard reflections were measured every 50 reflections as orientation and intensity control and no significant intensity decay was observed. The intensities were corrected for Lorentz and polarization but not for absorption effects. The scattering factors were taken from ref. 19.

The initial crystallographic positions of the Cr, Cu, N and Cl atoms were taken from the structure of $[Cr(NH_3)_6][CuCl_5]$ [15]. The N site was assumed to be occupied 5/6 by N and 1/6 by O. The first isotropic refinement using SHELX76 [20] gave values of $R = 0.125$ and $R_w = 0.141$, and by introducing anisotropic thermal parameters the agreement factors were lowered to 0.048 and 0.063 respectively. At this point the three ammonia hydrogen were located and introduced in the refinement with fixed occupancies equal to unity and identical isotropic thermal parameters. After this model converged, the occupancies of H1 and H2 were allowed to refine, keeping the occupancy of H3 equal to one, since this hydrogen is involved in a strong hydrogen bond and is assumed to be also a water hydrogen site. The model converged for occupancies of 0.96 and 0.69 for H1 and H2 respectively. Therefore occupancies of H1 and H3 were fixed equal to one, assuming that both sites correspond either to ammonia or to water hydrogens, while the H2 occupancy was fixed to 5/6, considering that this site corresponds only to an ammonia hydrogen. The final values for the agreement factors were $R = 0.036$ and $R_w = 0.045$. It should be pointed out that both values were only slightly sensitive to the hydrogen occupancies.

X-ray Powder diffraction Data

The spectra were collected on a Siemens D-500 diffractometer with a Cu X-ray target operated at 20 mA and 40 kV using a graphite monochromator, scintillation counter and a conventional pulse height electronics. A wavelength of 1.54059 Å was used in all calculations. Data collection was performed under computer control (DEC PDP 11/34) using the commercial SIEMENS DIFFRAC-11/2 software package through DACO-MP interface, which uses the VISSOR [21] cell indexing program and the APPLEMAN [22] cell refinement program. NaCl was added to the sample and used as d-spacing standard.

Results and Discussion

Spectral Measurements

The IR bands corresponding to the coordinated NH_3 group appear at the expected frequencies [23]. In addition, the hexacyanometallate(III) complexes exhibit bands assigned to the CN ligand. The most characteristic band is due to the ν(CN) mode which appears in the range 2115–2135 cm^{-1} in all cases. This band is sensitive to the hydrogen bonds in the crystalline cell [24, 25].

The insolubility of the hexacyanometallate(III) complexes does not allow their electronic spectra in solution to be registered. The pentachlorocuprate-(II) complexes are soluble, but the $[CuCl_5]^{3-}$ anion decomposes in aqueous solution giving different aqua species. In all cases the electronic spectra taken from aqueous solution show a broad band centered at 800 nm that can be assigned to the hydrolyzed Cu(II) ion [26]. On the other hand, the compounds containing amminated or aquo-amminated cations display the bands expected for these stable species in aqueous solution.

Molecular and Crystalline Structure of $[Cr(H_2O)(NH_3)_5][CuCl_5]$

The fractional atomic coordinates with their estimated standard deviations are listed in Table 1. Figure 1 shows a view of the molecular structure with the atom numbering scheme used. Selected bond distances and angles are given in Table 2. Cell parameters are given in Table 3.

The crystals belong to the cubic space group *Fd3c* and the structure consists of pseudooctahedral $[Cr(H_2O)(NH_3)_5]^{3+}$ cations and what appears to be trigonal bipyramid $[CuCl_5]^{3-}$ anions connected by hydrogen bonds. These anions present striking features that are commented on below. The presence of the $[Cr(H_2O)(NH_3)_5]^{3+}$ cations of local symmetry C_{4v} in a 3 symmetry site in the cubic cell indicates disorder in the location of the H_2O group around the Cr(III) ion. The H_2O molecule occupies statistically 1/6 of the coordination sites in the octahedron. The same situation has been found in $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$ [10] isostructural with $[Co(NH_3)_6][Cr(CN)_6]$ [6, 7].

The coordination polyhedron around the Cr(III) ion is a slightly distorted octahedron. The N(O)–Cr–N(O) angle is 89.4° identical to the one found in $[Cr(NH_3)_6][Cr(CN)_6]$ [15]. The average Cr–N

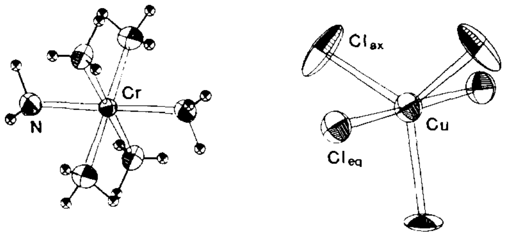

Fig. 1. Molecular structure of $[Cr(H_2O)(NH_3)_5][CuCl_5]$.

TABLE 1. Fractional coordinates ($\times10^{-4}$; $\times10^{-3}$ for hydrogen) with e.s.d.s in parentheses

	x/a	y/b	z/c
N(O)	305(2)	−707(2)	−515(2)
Cu	2500	2500	2500
Cr	0	0	0
Cl$_{ax}$	1900(1)	1900(1)	1900(1)
Cl$_{eq}$	2500	760(1)	9240(1)
H1	7(3)	−93(4)	−57(4)
H2	68(4)	88(4)	−42(5)
H3	43(4)	58(4)	92(4)

TABLE 2. Selected bond distances (Å) and angles (°)

Cr–N(O)	2.058(5)	N(O)–Cr–N(O)	89.4(2)
N(O)–H1	0.72(7)	Cr–N(O)–H1	112(7)
N(O)–H2	0.95(9)	Cr–N(O)–H2	118(6)
N(O)–H3	0.99(9)	Cr–N(O)–H3	112(4)
$Cu–Cl_{ax}$	2.309(3)	H1–N(O)–H2	113(9)
$Cu–Cl_{eq}$	2.388(3)	H1–N(O)–H3	104(8)
$H3...Cl_{eq}$	2.34(3)	H2–N(O)–H3	94(7)
$H2...Cl_{eq}$	2.54(3)		
$H1...Cl_{ax}$	2.63(3)		

bond is 2.058 Å, slightly shorter than in the compound $[Cr(NH_3)_6][CuCl_5]$ (2.064 Å). The difference is probably due to the shorter Cr–O bond and the disorder in the location of the H_2O group already mentioned.

The coordination around the Cu(II) ion is less clear. X-ray data seem to indicate that the Cu(II) ion is located on a D_3 site and the geometry around it is a regular trigonal bipyramid with three equatorial Cu–Cl bond distances at 2.388 Å and two axial spacings at 2.309 Å. These two bond lengths are in the range of the ones found in other pentachlorocuprate(II) compounds [14, 15]. Moreover, the anisotropic thermal parameters are anomalously high for the equatorial Cl atoms [$U11 = 1703(37)$; $U22 = U33 = 319(9)$ $(\times 10^{-4})$] compared with the same parameters for the axial Cl atoms [$U11 = U22 = U33 = 417(8), \times 10^{-4}$)].

The same situation occurs in the better studied isomorphous compound $[Co(NH_3)_6][CuCl_5]$. From the analysis of EPR spectra and powder diffraction diagrams as a function of temperature a model based on a dynamic average of three square-pyramidal conformations has been proposed [27]. A mechanism of pseudo-rotation would transform the square-pyramids in each other. Specific heats and magnetic studies have recently supported the model [17].

The most important interionic interaction is the hydrogen bond between H(3) and Cl(eq.) (2.34 Å). The distance N–Cl(eq.) is 3.30 Å and the N–H(3)–Cl(eq.) angle is 164°. These interactions are responsible for the magnetic behaviour at low temperatures found in this compound [5b].

X-ray Diffraction Powder Data

The behaviour is identical in both series. X-ray diffraction powder diagrams for these compounds in each series are similar, showing small shifts in the observed lines. All compounds in each series are isostructural and a disorder in the location of the H_2O groups in the coordination sites of the cation is assumed.

Conclusions

The cations $[M(NH_3)_6]^{3+}$, $[M(H_2O)(NH_3)_5]^{3+}$ and $[M(H_2O)_2(NH_3)_4]^{3+}$ (M = Co or Cr) yield isostructural compounds when the same complex anion ($[CuCl_5]^{3-}$ or $[M(CN)_6]^{3-}$) is present. The presence of voluminous cations and anions give relatively simple structures with high symmetry in which both ions are connected by hydrogen bonds. These structures generally exhibit interesting magnetic properties [4]. The isostructuralism in these compounds is probably due to the observed disorder in the H_2O ligand group position.

Supplementary Material

Fully indexed powder diagrams for all fifteen compounds (15 pages) and Tables for observed

TABLE 3. Cell parameters

Compound	*a* (Å)	α (°)	a^3 (Å^3)
$[Co(NH_3)_6][CuCl_5]$	22.079(3)		10763.9(3)
$[Co(H_2O)(NH_3)_5][CuCl_5]$	21.966(4)		10599.2(3)
$[Co(H_2O)_2(NH_3)_4][CuCl_5]$	21.844(3)		10423.2(4)
$[Cr(NH_3)_6][CuCl_5]$	22.270(4)		11045.1(4)
$[Cr(H_2O)(NH_3)_5][CuCl_5]$	22.181(3)		10912.9(3)
$[Co(NH_3)_6][Co(CN)_6]$	7.284(4)	97.93(3)	373.2(4)
$[Co(H_2O)(NH_3)_5][Co(CN)_6]$	7.242(4)	97.42(2)	368.7(5)
$[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$	7.153(3)	97.15(3)	354.1(2)
$[Cr(NH_3)_6][Co(CN)_6]$	7.295(3)	97.34(3)	376.4(3)
$[Cr(H_2O)(NH_3)_5][Co(CN)_6]$	7.241(3)	97.37(2)	370.0(3)
$[Cr(H_2O)_2(NH_3)_4][Co(CN)_6]$	7.212(3)	97.28(4)	365.0(4)
$[Co(NH_3)_6][Cr(CN)_6]$	7.414(4)	98.02(3)	393.1(5)
$[Co(H_2O)(NH_3)_5][Cr(CN)_6]$	7.383(3)	100.71(4)	377.9(3)
$[Cr(NH_3)_6][Cr(CN)_6]$	7.475(4)	97.76(2)	404.4(3)
$[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$	7.412(3)	97.65(3)	406.9(4)

and calculated structure factors and anisotropic thermal parameters (2 pages) are available from the authors on request.

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