

The Structure of the Solid Solution $(\text{Me}_4\text{N})_2(\text{Cu}_{0.51}\text{Co}_{0.49})\text{Cl}_4$

BY ROBERT M. CLAY, JUDITH MURRAY-RUST AND PETER MURRAY-RUST

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

(Received 27 May 1975; accepted 29 May 1975)

A single crystal with composition $[\text{N}(\text{CH}_3)_4]_2(\text{Cu}_{0.51}\text{Co}_{0.49})\text{Cl}_4$ has been prepared and investigated by X-ray diffraction. The compound is a solid solution of $(\text{Me}_4\text{N})_2\text{CuCl}_4$ and $(\text{Me}_4\text{N})_2\text{CoCl}_4$, and is isomorphous with these, crystallizing in space group $Pnma$ with $a = 12.30$, $b = 9.04$, $c = 15.52$ Å. Intensities were collected photographically with Mo $K\alpha$ radiation and measured visually for 667 independent reflexions. Three models for the structure were considered, the one most acceptable having a final R of 0.083. This model consisted of an average 'host lattice' of $\text{N}(\text{CH}_3)_4^+$ cations with a random distribution of CuCl_4^{2-} and CoCl_4^{2-} on the anion sites. These anions have essentially the same geometries as in their respective parent compounds $[(\text{Me}_4\text{N})_2\text{MCl}_4; \text{M} = \text{Cu}, \text{Co}]$ but have undergone translations towards their common centre of gravity in the solid solution.

Introduction

The use of dilute solid solutions to permit the measurement of the spectroscopic properties of ions is well known, for example, the solution of CuCl_4^{2-} (tetrahedral) in Cs_2ZnCl_4 (Gruen & McBeth, 1963). Dilute (1–5%) solid solutions are usually used for these measurements, but it is sometimes possible to make a complete composition range of the solid solution of two isomorphous compounds. Phase diagrams have been determined for $(\text{Me}_4\text{N})_2\text{M}'\text{Cl}_4 - (\text{Me}_4\text{N})_2\text{M}''\text{Cl}_4 - \text{solvent}$ where M' , M'' were any pair from Co^{2+} , Cu^{2+} , Zn^{2+} and the solvent was water, ethanol or 50% v/v water-ethanol (Murray-Rust, 1971). For a system of two salts and a solvent (in which a continuous series of solid solutions is formed) the proportion of each salt present in the liquid phase at equilibrium is determined by the free energy of solution of the solid phase. If this is a linear function of the mole fraction of either salt in the solid solution, then (Roozeboom, 1891) for the salt which is more soluble in the particular solvent, a plot of mole fraction of that salt in the solute against mole

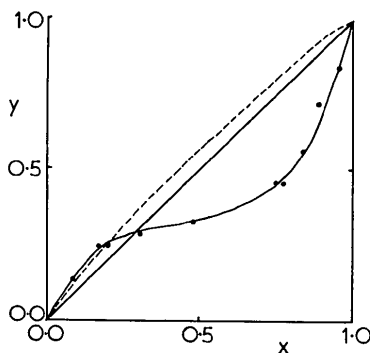


Fig. 1. Roozeboom plot for $(\text{Me}_4\text{N})_2\text{CuCl}_4 - (\text{Me}_4\text{N})_2\text{CoCl}_4 - \text{H}_2\text{O}$ at room temperature. x = mole fraction of $(\text{Me}_4\text{N})_2\text{CuCl}_4$ in the solid solution; y = mole fraction of $(\text{Me}_4\text{N})_2\text{CuCl}_4$ in the solute (liquid phase). Experimental points are marked \bullet ; the dashed line is the curve expected from the ratio of the solubilities in water of the two end compounds.

fraction in the solid solution will have the form shown in Fig. 1 (dotted line). This means that the composition of the solid solution in equilibrium with a given liquid phase depends only on the solubility ratio of the two salts. The Roozeboom plot found experimentally for $(\text{Me}_4\text{N})_2\text{CuCl}_4 - (\text{Me}_4\text{N})_2\text{CoCl}_4 - \text{water}$ does not fit this simple model, but suggests that ΔG_{sol} is a non-linear function of the molar ratio. Qualitatively, Fig. 1 implies that it is more difficult to place CuCl_4^{2-} than CoCl_4^{2-} into a solid solution with high $(\text{Me}_4\text{N})_2\text{CoCl}_4$ concentration. The reasons for this may be found in either the liquid or solid phase properties of the ions. In the liquid phase there will be equilibrium between octahedral ($\text{H}_2\text{O} + \text{Cl}^-$) and tetrahedral (Cl^-) coordination of the metal ions, and it is not easy to follow the changes in the coordination of the metals as the composition of the solution varies. In the solid phase the stoichiometry of the individual anions is fixed, but the overall composition may be affected by differences in ionic size, ionic shape, or in the relative ease with which the guest ions and host lattice adjust to accommodate each other. A crystal structure determination of a solid solution can be used to investigate whether there are changes in the anionic geometries from those found in the two end compounds. Hatfield & Piper (1964) have already suggested from spectroscopic evidence that the degree of D_{2d} distortion of CuCl_4^{2-} in solid solution in Cs_2ZnCl_4 increases with concentration of the Cu^{2+} ion.

The crystal structures of $(\text{Me}_4\text{N})_2\text{CoCl}_4$ (Wiesner, Srivastava, Kennard, Di Vaira & Lingafelter, 1967) and $(\text{Me}_4\text{N})_2\text{CuCl}_4$ (Clay, Murray-Rust & Murray-Rust, 1975) are known ($R = 0.111$ and 0.075 respectively); they are isostructural, crystallizing in space group $Pnma$ with approximate cell dimensions $a = 12.3$, $b = 9.0$ and $c = 15.5$ Å. * Both MCl_4^{2-} ions are distorted

* A slight complication in the comparison of these structures might arise from the presence in the Cu compound of very weak reflexions indicating a tripling of a . This was suggested to be a result of disorder in the cation positions (Morosin & Lingafelter, 1961) but has not yet been fully interpreted.

(D_{2d}) from T_d symmetry, but the distortion of CuCl_4^{2-} is much greater than CoCl_4^{2-} (the largest Cl-M-Cl angle is 132° in CuCl_4^{2-} and 112° in CoCl_4^{2-}). For the structure of a 50:50 solid solution, two simple models can be proposed. In the first each ion retains its 'characteristic' degree of distortion shown in the end compound, and in the second the ions adopt intermediate geometries in response to lattice forces. We report the crystal structure analysis of this intermediate compound, and its compatibility with these models.

Experimental

Preparation of the compounds

$(\text{Me}_4\text{N})_2\text{CuCl}_4$ and $(\text{Me}_4\text{N})_2\text{CoCl}_4$ were prepared by precipitation from a concentrated ethanolic solution of the constituent chlorides in stoichiometric amounts, and the products recrystallized from water.

$(\text{Me}_4\text{N})_2(\text{Cu},\text{Co})\text{Cl}_4$ was prepared by equilibration of $(\text{Me}_4\text{N})_2\text{CuCl}_4$, $(\text{Me}_4\text{N})_2\text{CoCl}_4$ and water at room temperature, in quantities chosen from the phase diagram for the system (Murray-Rust, 1971) to give a Cu:Co ratio close to unity. The resultant crystalline solid solution had a Cu:Co ratio for the bulk product of 51:49 (from atomic absorption analyses for Cu^{2+} and Co^{2+}). Microscopic examination of sections of a number of the crystals failed to reveal any gross inhomogeneities.

Crystal data

$\text{C}_8\text{H}_{24}\text{Co}_{0.49}\text{Cu}_{0.51}\text{Cl}_4\text{N}_2$, $M=352$ (approx.). Orthorhombic, space group $Pnma$ (from systematic absences $hk0$, h odd and $0kl$, $k+l$ odd), $a=12.30$, $b=9.04$, $c=15.52$ Å (from Weissenberg and oscillation photographs, estimated error 2%). Approximate crystal dimensions $0.3 \times 0.3 \times 0.25$ mm.

No evidence of superlattice formation (particularly the tripling of a already mentioned) was found from any of the preliminary photographs.

Data were collected for layers $h0-5l$ and $0-2kl$ with Mo $K\alpha$ radiation and a multiple-film Weissenberg technique. Intensities were estimated visually by comparison with a calibrated strip. Lorentz and polarization, but no absorption or spot-shape corrections were applied, and after scaling and merging, 667 independent reflexions were obtained and placed on an absolute scale by a Wilson plot.

Analysis of the structure

Both $(\text{Me}_4\text{N})_2\text{CuCl}_4$ and $(\text{Me}_4\text{N})_2\text{CoCl}_4$ had been shown to be in the space group $Pnma$, and this was assumed for the solid solution. Since refinement proceeded satisfactorily in the centrosymmetric space group, the possible non-centrosymmetric space group $Pn2_1a$ was not further considered.

Since the crystal structures of $(\text{Me}_4\text{N})_2\text{CuCl}_4$ and $(\text{Me}_4\text{N})_2(\text{Cu},\text{Co})\text{Cl}_4$ were both analysed in our laboratory, whereas that of $(\text{Me}_4\text{N})_2\text{CoCl}_4$ was done elsewhere, spurious differences in the parameters might

arise from differences in the treatment of unobserved reflexions or in the weighting schemes. The structure of $(\text{Me}_4\text{N})_2\text{CoCl}_4$ was therefore re-refined with Wiesner's data, but no significant differences ($>2\sigma$) in any of the parameters were found.

Wiesner's positional parameters for $(\text{Me}_4\text{N})_2\text{CoCl}_4$, and estimated isotropic temperature factors, were used as the starting point for the refinement of the solid solution structure. Scattering factors were taken from *International Tables for X-ray Crystallography* (1968) except for the metal ion, which was given an average scattering factor $f_{av}=0.5f_{\text{Cu}^{2+}}+0.5f_{\text{Co}^{2+}}$. Refinement was by full-matrix least-squares calculations, using our adaptation of the *PORFLS* system (Powell & Griffiths, 1969), minimizing $w\Delta^2$, and using the weighting scheme $w=1$ for $F < 25$, $w=1/[F-\{(F-25)/60\}^2]$ for $F \geq 25$. Unobserved reflexions were excluded.

Seven cycles of refinement of positional and isotropic thermal parameters converged at $R=\sum|F_o|-|F_c|/\sum F_o$, and one cycle including anisotropic thermal parameters gave $R=0.125$. Three different models were then used to find the best description of the structure, and these are given below.

(i) Refinement of the average structure above, *i.e.* with one set of parameters per atom and site occupancies of 1.0. Full-matrix refinement of positional and anisotropic thermal parameters converged at $R=0.089$. We now recognize the following groups of atomic parameters: $p_i(\text{Co})$, the parameters in $(\text{Me}_4\text{N})_2\text{CoCl}_4$, $p_i(\text{Cu})$ in $(\text{Me}_4\text{N})_2\text{CuCl}_4$ and $\bar{p}_i(\text{CuCo})$ in the average structure of the solid solution as described in (i). Fig. 2 is a plot (for the positional parameters) of $[\bar{p}_i(\text{CuCo})-p_i(\text{Cu})]$ against $[p_i(\text{Co})-p_i(\text{Cu})]$. It suggests that the average atomic positions in the solid solution can be fairly well found by a composition-weighted linear interpolation between $p_i(\text{Co})$ and $p_i(\text{Cu})$.

(ii) A better model for the solid solution might be obtained by allowing each atomic position in the cell to have two sets of parameters, $p_{ia}(\text{CuCo})$ and $p_{ib}(\text{CuCo})$, with site occupancy 0.5, and refining these sets separately. (The occupancy is a result of the stoi-

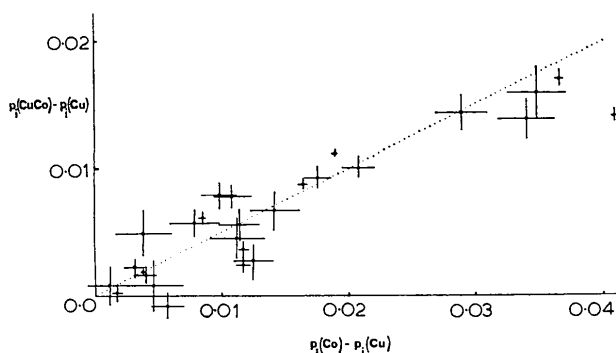


Fig. 2. A comparison of the fractional coordinates of $(\text{Me}_4\text{N})_2\text{MCl}_4$ ($M=\text{Cu},\text{Co}$) [$p_i(\text{Cu}), p_i(\text{Co})$] with those of $(\text{Me}_4\text{N})_2(\text{Cu}_{0.51}\text{Co}_{0.49})\text{Cl}_4$ [$\bar{p}_i(\text{CuCo})$] from the average structure, model (i). Error bars = 1 e.s.d.; the dotted line is that expected for an average structure containing Cu:Co = 50:50.

chiometry, not a refinable parameter.) The initial values of $p_{ia}(\text{CuCo})$ and $p_{ib}(\text{CuCo})$ were $p_i(\text{Co})$ and $p_i(\text{Cu})$ respectively. The sets $p_{ia}(\text{CuCo})$ and $p_{ib}(\text{CuCo})$ could not be refined simultaneously, since near singularities in the matrix would certainly be caused, so they were refined in two separate cycles. This procedure bears the danger that no interaction between $p_{ia}(\text{CuCo})$ and $p_{ib}(\text{CuCo})$ is allowed, and that consequently the initial model might remain essentially unchanged. The significance of the result after doubling the number of parameters must also be examined carefully. The final R after refinement of this model was 0.082.

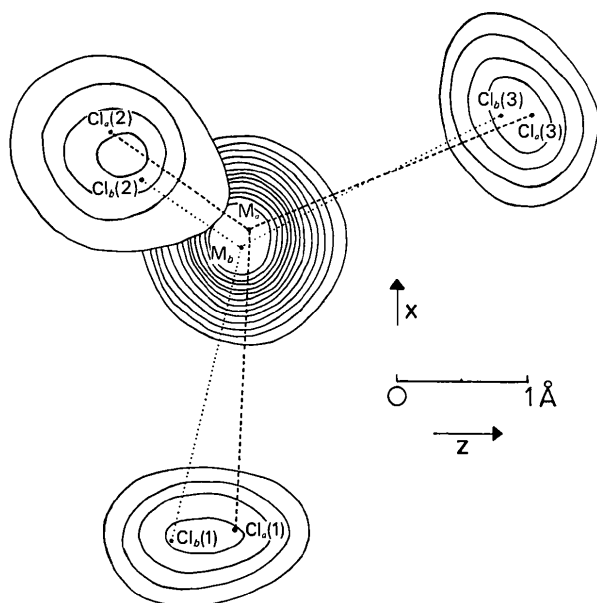


Fig. 3. A composite ac projection of the electron density in the anion at $y = \frac{1}{2}$, [Cu, Co, Cl_a(1), Cl_b(1), Cl_a(3), Cl_b(3)] and $y = \frac{1}{3^2}$, [Cl_a(2), Cl_b(2)]. The contours are at equal arbitrary intervals. The dotted and dashed lines represent Cu-Cl and Co-Cl bonds respectively.

(iii) In this set of compounds, the parameters of the light atom tetrahedra are not as accurately known as those of the MCl_4^{2-} tetrahedra, and so a compromise model was also refined, with a light-atom 'host lattice' in which the two types of MCl_4^{2-} tetrahedra are placed. The parameters were, for the light atoms (L), $\bar{p}_i(\text{CuCo})_L$ with occupancy 1.0, and for the heavy atoms (H), $p_{ia}(\text{CuCo})_H$ and $p_{ib}(\text{CuCo})_H$, with occupancy 0.5. [$\bar{p}_i(\text{CuCo})_L$ and $p_{ia}(\text{CuCo})_H$] and [$\bar{p}_i(\text{CuCo})_L$ and $p_{ib}(\text{CuCo})_H$] were refined in separate cycles. Thus, although $p_{ia}(\text{CuCo})_H$ and $p_{ib}(\text{CuCo})_H$ could not interact directly, any gross changes could affect $\bar{p}_i(\text{CuCo})_L$ and be transmitted indirectly to $p_{ib}(\text{CuCo})_H$ or $p_{ia}(\text{CuCo})_H$. The final R after this calculation was 0.083.

The Hamilton (1965) tests were used to check the significance of the changes in final R with the increased numbers of parameters used in (ii) and (iii). Model (ii) was found to be significant only at the 5–10% level, whereas (iii) was significant at the 1% level. On this basis (iii) gave the best parameters for the solid solution, and these are listed in Table 1.* The meaningfulness of these parameters can be questioned on the basis of the refinement procedure taken by itself, but we show in the *Discussion* that the positional shifts that occurred in (iii) [e.g. the differences between $p_i(\text{Co})$ and $p_{ia}(\text{CuCo})$] are consistent with rigid-body translations of the MCl_4^{2-} tetrahedra.

Discussion

Fig. 3 is a sketch of the electron density in sections through the anion from an F_o map phased on the final parameters from refinement (iii), with the positions of the atomic centres indicated. During the analysis the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31170 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic positions ($\times 10^4$) and anisotropic temperature factors ($\times 10^4$)

E.s.d.'s are given in parentheses. β_{11} etc. are the coefficients in the expression for the anisotropic temperature factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	2424 (4)	2500	4064 (3)	93 (5)	166 (9)	57 (3)	*	2 (3)	*
Cl _{Co} (1)	597 (10)	2500	4016 (12)	78 (8)	328 (30)	108 (11)	*	-6 (9)	*
Cl _{Co} (2)	3019 (10)	431 (12)	3402 (7)	131 (9)	210 (17)	101 (5)	31 (11)	24 (5)	-57 (8)
Cl _{Co} (3)	3134 (13)	2500	5451 (9)	189 (16)	364 (31)	54 (7)	*	-21 (8)	*
Cu	2315 (4)	2500	4038 (3)	73 (4)	147 (7)	51 (2)	*	0 (3)	*
Cl _{Cu} (1)	513 (11)	2500	3702 (12)	91 (9)	313 (30)	87 (9)	*	-11 (7)	*
Cl _{Cu} (2)	2735 (11)	271 (13)	3556 (10)	150 (13)	169 (18)	225 (13)	39 (13)	-41 (11)	-48 (12)
Cl _{Cu} (3)	3123 (13)	2500	5301 (10)	176 (14)	614 (49)	48 (7)	*	-30 (8)	*
N(1)	1406 (11)	2500	936 (10)	85 (11)	192 (30)	65 (8)	*	24 (9)	*
N(2)	5019 (13)	2500	8279 (10)	112 (15)	211 (34)	60 (9)	*	1 (10)	*
C(1)	2592 (18)	2500	1050 (19)	99 (21)	400 (74)	159 (23)	*	-24 (19)	*
C(2)	1122 (26)	2500	23 (18)	208 (37)	768 (127)	75 (15)	*	-42 (20)	*
C(3)	957 (19)	3805 (26)	1399 (16)	235 (27)	317 (48)	219 (22)	100 (29)	37 (19)	-154 (30)
C(4)	4380 (27)	2500	7476 (18)	261 (41)	502 (84)	81 (14)	*	-65 (21)	*
C(5)	4306 (28)	2500	9018 (18)	210 (39)	1130 (190)	68 (16)	*	0 (21)	*
C(6)	5626 (23)	3867 (30)	8367 (19)	353 (41)	353 (57)	249 (26)	-249 (42)	-130 (28)	116 (33)

* $\beta_{12} = \beta_{23} = 0$ by symmetry.

parameters $p_{ia}(\text{CuCo})_H$ and $p_{ib}(\text{CuCo})_H$ were refined in separate cycles, but these atomic groupings did not necessarily correspond to actual chemical entities. There are, however, some indications from the interatomic distances within the anions (Table 2) as to which metal and Cl ions might reasonably be bonded to one another. $M_a\text{-Cl}_b(1)$ and $M_b\text{-Cl}_a(3)$ are much longer, and $M_a\text{-Cl}_b(3)$ and $M_b\text{-Cl}_a(1)$ correspondingly much shorter than either Cu-Cl or Co-Cl bonds in this type of compound, so that for atoms lying in the $y = \frac{1}{4}$ mirror plane the most likely combinations are $M_a\text{-Cl}_a(1)$, $M_a\text{-Cl}_a(3)$, and $M_b\text{-Cl}_b(1)$, $M_b\text{-Cl}_b(3)$. The respective Cl(1)-M-Cl(3) angles for these two groups are 114.0° and 130.1° , which are close to the values found for the same atoms in $(\text{Me}_4\text{N})_2\text{CoCl}_4(112.6^\circ)$ and $(\text{Me}_4\text{N})_2\text{CuCl}_4(132.1^\circ)$. This leaves only the Cl(2) atoms. It is crystallographically conceivable (although unlikely) that neither of the MCl_4^- tetrahedra has m symmetry, and that Cl(2) and Cl(2') belong to two

different anions, but this results in unacceptable bond angles (119°) in both CuCl_4^- and CoCl_4^- . If it is assumed that each tetrahedron retains a mirror plane, then $\text{Cl}_a(2)\text{-M}_a\text{-Cl}_a(2') = 112.3^\circ$ and $\text{Cl}_b(2)\text{-M}_b\text{-Cl}_b(2') = 131.8^\circ$, which, like the distances and angles in the mirror plane, indicates $M_a = \text{Co}$ and $M_b = \text{Cu}$. The parameters $p_{ia}(\text{CuCo})_H$ and $p_{ib}(\text{CuCo})_H$ will therefore be relabelled $p_{\text{Co}}(\text{CuCo})$ and $p_{\text{Cu}}(\text{CuCo})$. The MCl_4^- tetrahedra in the solid solution now closely resemble those in the respective pure compounds, with CoCl_4^- having a small D_{2d} distortion and CuCl_4^- a much greater one; the average anion bond lengths in the solid solution are 2.27 in CoCl_4^- and 2.23 Å in CuCl_4^- . The full list of bond lengths and angles in the title compound is in Table 3.

Examination of the x and z parameters of MCl_4^- , $p_i(\text{Cu})$, $p_i(\text{Co})$, $p_{\text{Cu}}(\text{CuCo})$ and $p_{\text{Co}}(\text{CuCo})$ (*i.e.* the positions of CuCl_4^- and CoCl_4^- in the solid solution before and after refinement), shows systematic shifts of the tetrahedra. Both CuCl_4^- and CoCl_4^- have undergone a rigid-body translation towards their common centre of gravity (the Cu-Co separation decreased from 0.24 to 0.14 Å), with negligible rotational movement and the slight changes in geometry mentioned previously. The consistency of these shifts, together with the evidence of the Hamilton test, leads us to believe that refinement (iii) has a given meaningful improvement over (i) for the description of the structure of the solid solution.

Table 2. Interatomic distances within the two anions (Å)

$M_a - M_b = 0.14$			
$M_a\text{-Cl}_a(1)$	2.25	$M_b\text{-Cl}_a(1)$	2.11
$M_a\text{-Cl}_b(1)$	2.42	$M_b\text{-Cl}_b(1)$	2.28
$M_a\text{-Cl}_a(2)$	2.26	$M_b\text{-Cl}_a(2)$	2.29
$M_a\text{-Cl}_b(2)$	2.25	$M_b\text{-Cl}_b(2)$	2.21
$M_a\text{-Cl}_a(3)$	2.32	$M_b\text{-Cl}_a(3)$	2.41
$M_a\text{-Cl}_b(3)$	2.10	$M_b\text{-Cl}_b(3)$	2.20

Average Cu-Cl distance in $(\text{Me}_4\text{N})_2\text{CuCl}_4 = 2.23$.
Average Co-Cl distance in $(\text{Me}_4\text{N})_2\text{CoCl}_4 = 2.25$.

Table 3. Bond distances (Å) and angles ($^\circ$) in $(\text{Me}_4\text{N})_2(\text{Cu}_{0.51}\text{Co}_{0.49})\text{Cl}_4$

In CoCl_4^-			
Co-Cl(1)	2.25 (1)	Cl(1)-Co-Cl(2)	107.9 (0.5)
Co-Cl(2)	2.26 (1)	Cl(1)-Co-Cl(3)	114.0 (0.4)
Co-Cl(3)	2.32 (1)	Cl(2)-Co-Cl(2')	112.3 (0.5)
		Cl(2)-Co-Cl(3)	107.6 (0.4)
In CuCl_4^-			
Cu-Cl(1)	2.28 (1)	Cl(1)-Cu-Cl(2)	98.1 (0.5)
Cu-Cl(2)	2.21 (1)	Cl(1)-Cu-Cl(3)	130.1 (0.4)
Cu-Cl(3)	2.20 (1)	Cl(2)-Cu-Cl(2')	131.8 (0.5)
		Cl(2)-Cu-Cl(3)	101.2 (0.4)
N(1)-C(1)	1.47 (3)	C(1)-N(1)-C(2)	111.1 (1.5)
N(1)-C(2)	1.45 (1)	C(1)-N(1)-C(3)	107.5 (1.4)
N(1)-C(3)	1.50 (3)	C(2)-N(1)-C(3)	112.7 (1.8)
		C(3)-N(1)-C(3')	105.1 (1.6)
N(2)-C(4)	1.48 (2)	C(4)-N(2)-C(5)	111.1 (2.0)
N(2)-C(5)	1.46 (3)	C(4)-N(2)-C(6)	110.5 (1.4)
N(2)-C(6)	1.47 (2)	C(5)-N(2)-C(6)	103.9 (1.2)
		C(6)-N(2)-C(6')	116.4 (1.3)

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