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Stepwise Formation of Fluoride Complexes of Chromium(III) in Mixed KSCN–KF Molten Salts

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The stepwise complexation of fluoride ions with Cr(III) in molten KSCN has been investigated at 185 °C. Absorption spectra of Cr(III) in KSCN–KF melts reveal a pronounced effect of selective fluoride association on the d-electron transitions. It is concluded that the octahedral Cr(III) coordination persists as the complexation proceeds. Fluoride activities were measured in the systems (K^+,Cr^{3+})–(SCN^-,F^-) by a recently developed potentiometric technique, utilizing a fluoride-selective membrane electrode. Ligand numbers between 0 and 3.2 were established, and the stability constants β_j for $Cr(NCS)_{6-j}F_j^{3-}$ have been determined for $1 \leqslant j \leqslant 4$. Higher ligand numbers cannot be achieved due to precipitation of K_3CrF_6 from the melts. It is demonstrated that the whole complexation process, involving four consecutive steps, can be successfully modeled by use of one single specific interaction energy parameter, ΔA, once the total coordination number of the acceptor ion is known. For the exchange Cr–NCS + F^- → Cr–F + NCS^- the best fitting value $\Delta A = -36.4$ kJ·mol^{-1} was obtained.

Introduction

Molten thiocyanates constitute an attractive class of ionic solvents for fundamental coordination chemistry studies. One reason for this is of course the ability of SCN^- to coordinate to metal ions either by the soft sulfur atom or by the harder nitrogen atom, depending on the acceptor character of the central ion. The general solvent properties of thiocyanate melts have been thoroughly reviewed by Kerridge.[1] Only a few quantitative studies of complex formation in molten KSCN seem to have been performed, however.[2–4]

In molecular solvents the main contribution to the free energy change for a typical a–a acceptor–donor association appears to be a large gain in configurational entropy due to desolvation of donor and acceptor ions. Formation of predominantly electrostatic bonds yields small negative or even positive enthalpy contributions to the free energy of complexation. In ionic melts such arguments are unlikely to hold. A strong complex association in typical ionic liquids with an inherent short-range order is generally considered to be due to a specific covalent interaction between central ion and ligand. The configurational entropy change for such a process is largely determined by the short-range ordering imposed by the requirement of charge alternation in the melt as a whole. If, however, the effective radii of equally charged anions, such as F^- and SCN^-, are considerably different, one might expect a free energy loss due to Coulomb effects upon changing SCN^- for F^- in the coordination sphere of a highly charged solute cation in an ionic liquid like KSCN–KF. This would thus lead to a nonrandom anion distribution, conventionally described as complex formation.

The present investigation was undertaken in order to gain insight into the association between a typical a-acceptor, Cr^{3+}, and F^- in the "soft" molten KSCN solvent. The main advantages of using the KSCN solvent are the relatively high solubility of KF (~0.5 mol·kg^{-1}) and the possibility of working at a comparably low temperature, in this case 185 °C. By use of the fluoride-selective membrane electrode, developed by us for work up to 200 °C,[5] it is possible to measure fluoride activities accurately in molten salts and hence to investigate a strong association of fluoride to metal ions in a quantitative way. Metal ion association with fluoride in ionic melts can thus be studied under experimental conditions that are much more favorable than those encountered in work with pure fluoride melts.

The first indication of complex formation in the system (K^+,Cr^{3+})–(SCN^-,F^-) was the visual observation of a melt containing chromium(III), losing most of its intense green color when fluoride ions were added. Electronic absorption spectroscopy was employed in an attempt to study the fluoride association quantitatively, but only a qualitative picture of the complexation could be obtained. More precise information about the thermodynamics of fluoride association with Cr(III) in KSCN is gained from the potentiometric measurements.

Experimental Section

Chemicals. KSCN (Merck, p.A.) was dried by heating at 120 °C for several days. The salt was then melted, passed through a medium-porosity glass filter at 190 °C, quenched, and stored in the form of lumps under a dry atmosphere prior to use. $K_3Cr(SCN)_6$ and KF (Fluka, p.A.) were dried at 120 °C for at least 24 h. All operations involving fluoride-containing chemicals were performed under a dry N_2 atmosphere in a glovebox.

Electronic Absorption Spectra. The spectra were recorded with a Unicam SP 700 instrument, modified for high-temperature work. The design and temperature control of the furnace compartment have been described earlier.[6] Weighed amounts of solidified stock melts of KSCN + $K_3Cr(SCN)_6$ and KSCN + KF were mixed with pure KSCN to give test melts of the desired composition. The mixture was melted, stirred, and transferred into 10-mm fused silica cells. Spectra were recorded between 400 and 700 nm with pure KSCN as reference.

Emf Measurements. The fluoride-selective membrane electrode used in the present investigation was a slightly modified version of the one previously described.[5] The electrode body was manufactured from Pyrex glass, so the internal melt of the electrode could be carefully examined by visual inspection before the entire cell was mounted.

A schematic description of the cell is

$$\begin{array}{c|l||l|l|l|c}
 & \mathrm{KSCN(l)} & \mathrm{KSCN(l)} & & \mathrm{KSCN(l)} & \\
\mathrm{Ag} & & \mathrm{KF} & \mathrm{LaF_3} & \mathrm{Ag_2SO_4(satd)} & \mathrm{Ag} \\
 & \mathrm{Ag_2SO_4(satd)} & \mathrm{K_3Cr(SCN)_6} & \quad\mathrm{membrane} & \mathrm{KF(satd)} &
\end{array}$$

Further details on furnaces, temperature control, cell construction, and measurements have been described elsewhere.[7–9]

The compositions of the test melts were varied by additions of KF and $K_3Cr(SCN)_6$ or solidified stock melts of KSCN + KF and KSCN + $K_3Cr(SCN)_6$. Stable emf readings (±0.1 mV) could then be obtained within 0.5 h after the melt composition had been changed. After each experimental run the membrane electrode was emptied and allowed to cool down to room temperature. The LaF_3 membrane was then removed from the electrode body and remounted onto a clean electrode body. This procedure was adopted since leaks appeared at the interface between membrane and electrode body upon thermal cycling. Because of this treatment of the fluoride electrode the system had to be recalibrated for each experimental series from potential measurements in pure KSCN–KF melts. The total fluoride concentration at the end of a calibration run was then used as the starting value of ligand concentration in the complex formation study. Cr(III) was added in portions until the fluoride activity decreased to about 10% of the starting value. KF was then added

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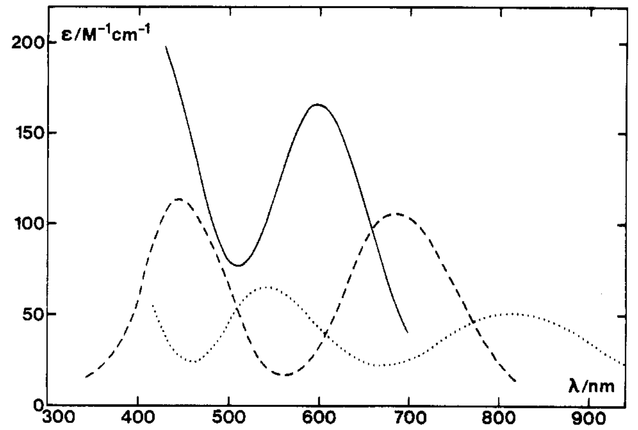

Figure 1. Electronic absorption spectra of chromium(III) in three different melts: (—) KSCN at 185 °C; (···) LiCl–KCl eutectic at 400 °C;[14] (- - -) LiF–NaF–KF eutectic at 650 °C.[15] The fluoride spectrum is considerably enhanced, but the absorbancies cannot be expressed on an absolute scale due to the experimental method used for recording the spectrum.[15]

Table I. Observed Absorption Maxima for the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ Transition in Molten KSCN, Ligand Field Strength Parameters *Dq*, and Molar Absorbances ε

λ/nm	Dq/cm^{-1}	ε/(M^{-1}·cm^{-1})	t/°C	ref
598	1672	167	185	this work
597.4	1673.9	191	185	10
600	1667	15 (?)	177	11
606	1650	128	200	12
549	1820	120	200	13
588[a]	1700	165	175	13

[a] Aqueous melt.

to a suitable amount, and Cr(III) was added again in successive steps and so forth. This procedure was adopted in order to obtain a maximum number of measured data during one experimental run.

The ranges of total concentrations covered were $6 \times 10^{-5} \leq C_{Cr}/(\text{mol·kg}^{-1}) \leq 2.3 \times 10^{-3}$ and $8.3 \times 10^{-4} \leq C_F/(\text{mol·kg}^{-1}) \leq 6.6 \times 10^{-3}$, and the measured free fluoride concentrations fell in the range $5.2 \times 10^{-5} \leq [F^-]/(\text{mol·kg}^{-1}) \leq 1.3 \times 10^{-3}$.

Each run normally lasted for 2 days. One day was used for the calibration of the electrode systems and 1 day for the complex formation measurements. The time of the measurements was not extended further due to small but significant changes of the emf when the system was left for longer periods of time. This slow drift in the emf was carefully examined during the calibration experiments and the extensive testing of the electrodes.[5] The maximum drift was about 0.4 mV/day. Since the measurements were performed as overlapping series, the very small effects of this drift vanish among the random errors that generate the confidence limits for the stability constants, stated in Table II.

Results and Discussion

Absorption Spectra. The spectrum of $K_3Cr(SCN)_6$ dissolved in molten KSCN at 185 °C is displayed in Figure 1. Spectra of clear green melts with a total concentration of chromium(III) ranging from 3.4×10^{-4} to 3.2×10^{-3} mol·kg^{-1} were recorded. From these spectra ε values were evaluated by use of a value of 1.60 g·cm^{-3} for the mass density of KSCN at 185 °C.[10]

The maximum of the band assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition for the octahedrally coordinated chromium(III) ion is positioned at 598 nm. This is in good agreement with previous investigations,[10-12] as can be seen from Table I. There is, however, a large spread in the reported ε values for this transition in the literature. Buryak and Volkov[13] assigned this band to the *trans*-$Cr(H_2O)_2(NCS)_4^-$ complex in aqueous melts, and the position of the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition in the anhydrous melts should be at 549 nm according to them. This interpretation seems doubtful to us. First, the melts studied by us certainly do not contain those large amounts of water that are required for the formation of $Cr(H_2O)_2(NCS)_4^-$. Second, the complete absence of the intense band in the high-energy region is in fact the most noteworthy feature of their spectra, which actually remains unexplained by their hypothesis.

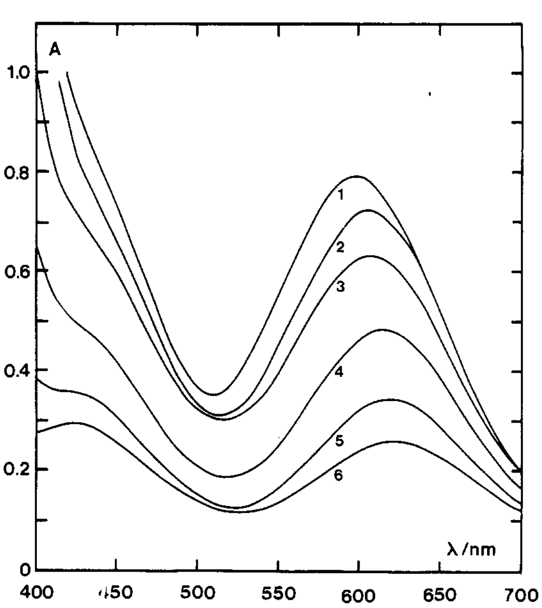

Figure 2. Absorption spectra of Cr(III) in molten KSCN at 185 °C recorded in a 10-mm cell. All melts have the same total chromium concentration, $C_{Cr} = 2.91 \times 10^{-3}$ mol·kg^{-1}. The total fluoride concentrations and average ligand numbers are as follows (spectrum number, $10^3\,C_F$/(mol·kg^{-1}), $\bar{n}$): 1, 0, 0; 2, 1.27, 0.42; 3, 3.10, 1.02; 4, 4.78, 1.56; 5, 7.17, 2.30; 6, 9.01, 2.82.

The band, assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition, that has been found in spectra of octahedrally coordinated Cr(III) in LiCl-KCl eutectic[14] (540 nm) and in LiF-NaF-KF eutectic[15] (448 nm) (Figure 1), is covered by the shoulder of a very intense band in the thiocyanate melt. The intensity of this band is far stronger than what might be expected from a d–d transition in an octahedral complex. This band is thus believed to be due to charge transfer.

The position of the band assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition is a direct measure of the strength of the octahedral ligand field felt by the chromium(III) ion in the different melts. The order of *Dq* for the ligands is $NCS^- > F^- > Cl^-$, and the thiocyanate ion is thus assumed to be bonded by the nitrogen end. This has also been concluded from IR studies of Cr(III) in KSCN melts and solids.[16-20]

The spectrum of $K_3Cr(SCN)_6$ dissolved in water at room temperature was recorded for comparison. In such a solution $Cr(NCS)_6^{3-}$ is the main absorbing species due to its high kinetic inertness at room temperature—all provided the spectrum is recorded soon after dissolution of the salt.[21,22] The absorption bands for the purple aqueous solution are shifted toward lower wavelengths as compared to these bands in pure thiocyanate melt spectra, the ligand field strength being about 100 cm^{-1} weaker in the KSCN melt. Thus the ligand field is strongly affected by the surroundings of the entire complex $Cr(NCS)_6^{3-}$.

When fluoride is added to a KSCN melt containing Cr(III), the intensities of the d–d transition bands are reduced and the bands are shifted toward lower energies. Figure 2 shows this

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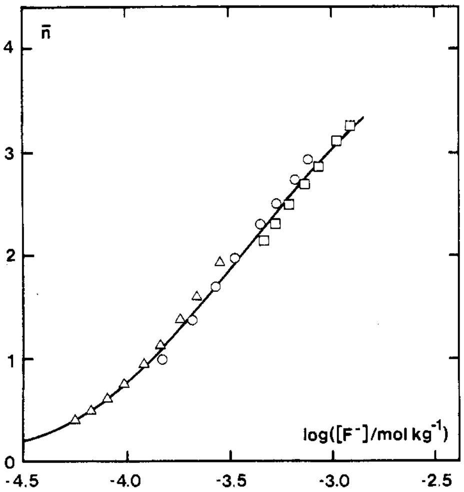

Figure 3. Typical experimental results from emf measurements of the fluoride activity. Experimentally determined $\bar{n}$ values from three different series are displayed, and the curve is constructed from eq 7 by use of the stability constants in Table II. The experimental data points are chosen to illustrate the typical spread in results and the extent of overlapping by different series.

behavior, which is a clear indication of fluoride complexation.

Because of the small shifts of the bands it was not possible to use the absorbance data for the determination of composition and stability of complex species. It is concluded, though, that the octahedral coordination geometry persists as the fluoride complexation proceeds. The average ligand numbers, $\bar{n}$, given in Figure 2, were calculated from the stability constants determined from the potentiometric data for the (K^+,Cr^{3+})–(SCN^-,F^-) systems.

Potentiometric Measurements. There is an excellent linear relation between the emf, E, for the fluoride electrode cell and log [F^-] in the range $3 \times 10^{-4} \leq C_F/(\mathrm{mol\cdot kg^{-1}}) \leq 5 \times 10^{-1}$. The emf can be expressed as[5]

$$E = E_0 - k \log ([\mathrm{F^-}]/(\mathrm{mol\cdot kg^{-1}})) \tag{1}$$

The experimentally determined slope k was found to differ slightly between different runs. Values between 91.6 and 95.6 mV were obtained. The experimental slopes are somewhat larger than the ideal one-electron value RTF^{-1} ln 10, 90.9 mV. The small discrepancies are most probably due to differences in the surface properties of the LaF_3 membranes used.

The experimental emf data were used to derive [F^-] from eq 1, and average ligand numbers $\bar{n}$ were thus obtained from

$$\bar{n} = (C_F - [\mathrm{F^-}])/C_{Cr} \tag{2}$$

C_F and C_{Cr} are total concentrations of fluoride and chromium(III), respectively.

Typical experimental results from three different series of measurements are displayed in Figure 3. It is noticeable that—although there is a small spread in the data—the ligand numbers do not depend on C_{Cr} but appear to be a function of [F^-] only. This means that only mononuclear complexes have to be considered in the data treatment.

Average ligand numbers higher than about 3.2 were unattainable due to precipitation of a greenish white solid. This precipitate was separated from the melt by filtration and washed with water. It was identified as K_3CrF_6 by X-ray powder diffraction. Since the potassium ion activity is practically constant in all investigated melts, a conditional solubility product K_s' for K_3CrF_6 can be expressed as

$$K_s' = [\mathrm{Cr^{3+}}][\mathrm{F^-}]^6 \tag{3}$$

K_s' was estimated at 185 °C to be $(2 \pm 1) \times 10^{-23}$ $\mathrm{mol^7\cdot kg^{-7}}$. This estimate was based on visual observations and spectrophotometric indication, i.e. a slightly raised base line as a faint precipitate appeared in the melt under study. [Cr^{3+}] and [F^-] in these melts were computed from known total concentrations and the final β values of Table II.

Table II. Overall and Stepwise Stability Constants for CrF_j^{3-j} in Molten KSCN at 185 °C[a]

j	$\beta_j/(\mathrm{mol^{-j}\cdot kg^{j}})$	$K_j/(\mathrm{mol^{-1}\cdot kg})$	$\beta_j^*/(\mathrm{mol^{-j}\cdot kg^{j}})$
1	$(5.3 \pm 1.2) \times 10^3$	5.3×10^3	8×10^3
2	$(4.0 \pm 0.5) \times 10^7$	7.4×10^3	3×10^7
3	$(4.3 \pm 1.4) \times 10^{10}$	1.1×10^3	5×10^{10}
4	$(5.7 \pm 0.7) \times 10^{13}$	1.3×10^3	5×10^{13}

[a] The error limits define a 95% confidence interval. The parameters β_j^* are obtained from model calculations (eq 12) with $\Delta A = -36.4$ $\mathrm{kJ\cdot mol^{-1}}$.

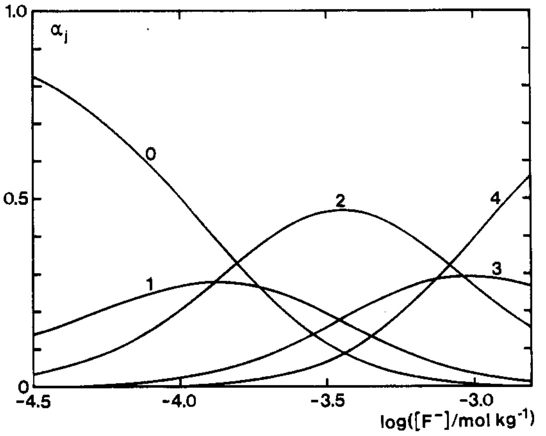

Figure 4. The fraction α_j of Cr(III) in different complexes $Cr(NCS)_{6-j}F_j^{3-}$ in molten KSCN at 185 °C. j is indicated on the curves.

It is clear from Figure 3 that formation constants for at least four consecutive complexation steps may be determined. The formation of CrF_j^{3-j} species can be described by a set of overall equilibria

$$\mathrm{Cr^{3+}} + j\mathrm{F^-} \rightleftarrows \mathrm{CrF}_j^{3-j} \tag{4}$$

where coordinated SCN^- ions have been omitted for the sake of clarity. The cumulative and stepwise stability constants β_j and K_j are expressed as

$$\beta_j = \frac{[\mathrm{CrF}_j^{3-j}]}{[\mathrm{Cr^{3+}}][\mathrm{F^-}]^j} \tag{5}$$

$$K_j = \frac{[\mathrm{CrF}_j^{3-j}]}{[\mathrm{CrF}_{j-1}^{3-j+1}][\mathrm{F^-}]} \tag{6}$$

For the final computation of the stability constants the least-squares program LIGANA was utilized. The program minimizes the sum $\sum(E_{\mathrm{exptl}} - E_{\mathrm{calcd}})^2$, containing the experimental and calculated emf's E_{exptl} and E_{calcd}, respectively. E_{calcd} is obtained from eq 1 and 2 and the expression

$$\bar{n}_{\mathrm{calcd}} = \frac{\sum_{j=1}^{4} j\beta_j[\mathrm{F^-}]^j}{1 + \sum_{j=1}^{4} \beta_j[\mathrm{F^-}]^j} \tag{7}$$

The calculations were based on a total of 215 points in the (C_{Cr}; C_F; E) space. The stability constants β_1–β_4 are given in Table II.

The fraction α_j of different species is defined as

$$\alpha_j = [\mathrm{CrF}_j^{3-j}]/C_{Cr} \tag{8}$$

Here α_0 is the fraction of $Cr(NCS)_6^{3-}$. Figure 4 shows the species distribution. Clearly, no single complex dominates in any composition region.

The quasi-lattice theoretical formalism[23] expresses the specific interaction energy ΔA_1 for the first ligand-exchange step through

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$$K_1 = Z[\exp(-\Delta A_1/RT) - 1] \qquad (9)$$

Here K_1 is expressed in mole fraction units, Z is the quasi-lattice coordination number, and ΔA_1 is the change in total acceptor-donor interaction energy, including the free energy contribution from changes in internal degrees of freedom for the thiocyanate ion. Analogous expressions can be derived for any step:

$$\mathrm{Cr(NCS)}_{Z-j+1}\mathrm{F}_{j-1}{}^{3-} + \mathrm{F}^- \rightarrow \mathrm{Cr(NCS)}_{Z-j}\mathrm{F}_j{}^{3-} + \mathrm{SCN}^-$$

In this system, where the complexation (i.e. the tendency to nonrandom anion distribution) is strong, it holds that $\exp(-\Delta A_j/RT) \gg 1$ for all values of j, so ΔA_j can be calculated according to

$$\Delta A_j = \Delta G^\circ{}_j + T[\Delta S^\circ{}_j(\mathrm{conf})] \qquad (10)$$

$\Delta S^\circ{}_j$(conf) is the ideal configurational entropy change, determined by the statistical probabilities of exchanging SCN$^-$ for F$^-$ in a fixed coordination sphere:

$$\Delta S^\circ{}_j(\mathrm{conf}) = R \ln \frac{Z - j + 1}{j} \qquad (11)$$

In view of the results from our study of ligand field spectra, it seems justified to use a value of 6 for Z. We calculated the total interaction energies ΔA_1–ΔA_4, and it appeared that all energy parameters fall in the range −36 ± 3 kJ·mol^{-1}.

The closeness of all ΔA_j values implies that the overall complexation process might be well described by the use of only one single specific interaction parameter ΔA independent of the number of fluoride ligands attached to the Cr(III) central ion. If so, the stability constants can be estimated through

$$\beta_j{}^* = \exp\left[\frac{-j(\Delta A)}{RT}\right] \frac{\prod_j (Z - j + 1)}{j!} \qquad (12)$$

In Table II the set of $\beta_j{}^*$ values, calculated with the best fitting value $\Delta A = -36.4$ kJ·mol^{-1} and $Z = 6$, are included for comparison. The agreement with experimentally determined β values is very good.

These results suggest that the estimated interaction energy may be of more general predictive value. It is thus important to extend the studies of fluoride complexation in mixed KSCN-KF melts to systems with other acceptor ions. Such studies are now in progress at our laboratory.

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Supplementary Material Available: A listing of experimental emf data (4 pages). Ordering information is given on any current masthead page.

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Magnetic Properties and Structural Characterizations of Bis(tetramethylammonium) Decachlorotetracuprate(II) and Bis(4-methyl-2-aminopyridinium) Decachlorotetracuprate(II)

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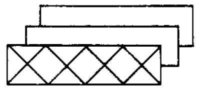
The crystal structures of bis(4-methyl-2-aminopyridinium) decachlorotetracuprate(II), $(4\mathrm{MAP})_2\mathrm{Cu_4Cl_{10}}$, and bis(tetramethylammonium) decachlorotetracuprate(II), $(\mathrm{TEMA})_2\mathrm{Cu_4Cl_{10}}$, have been determined. The 4MAP salt has a monoclinic structure [a = 3.847 (2) Å, b = 21.276 (2) Å, c = 15.336 (6) Å, β = 96.44 (3)°; space group $P2_1/n$; Z = 2] that contains discrete $(\mathrm{C_6N_2H_{10}})^+$ cations and pseudoplanar $(\mathrm{Cu_4Cl_{10}})^{2-}$ anions. The anions are centrosymmetric bibridged tetramers with each copper(II) ion exhibiting a 4 + 2 coordination geometry. The Cu–Cl distances within the tetramer average 2.285 Å with a range from 2.227 to 2.367 Å. The central Cu–Cl–Cu bridging bond angles are both 93.7°, while the outer pairs are 94.7 and 94.4°. The tetramers form stacks, I, parallel to the a axis, with each copper(II) ion completing its 4 + 2 coordination with chlorine atoms in adjacent



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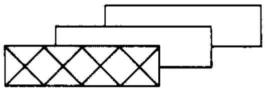

II

tetramers. The average intertetramer Cu–Cl bond distance is 2.987 Å. $(\mathrm{TEMA})_2\mathrm{Cu_4Cl_{10}}$ is monoclinic [a = 6.072 (2) Å, b = 19.574 (3) Å, c = 10.617 (3) Å, β = 99.46 (2)°; space group $P2_1/c$; Z = 2]. This structure also contains discrete $\mathrm{Cu_4Cl_{10}}^{2-}$ anions and $\mathrm{N(CH_3)_4}^+$ cations. The anions are similar to those of the 4MAP salt, with Cu–Cl distances ranging from 2.215 to 2.346 Å (2.276 Å average) and with central Cu–Cl–Cu angles of 93.5° and terminal angles of 93.6 and 95.5°. The tetramer stacks, II, yield a 4 + 1 coordination geometry for the two end copper(II) ions and a 4 + 2 coordination for the two central copper(II) ions. Magnetic susceptibilities for the salts were fitted to a nearest-neighbor Heisenberg exchange Hamiltonian for a linear tetramer, yielding values of −62.1 (2) K (4MAP) and −59.2 (9) K (TEMA) for the outer coupling constant, J_1/k, and a value of 36 (33) K (4MAP) and 26 (18) K (TEMA) for the central coupling constant, J_2/k.

Introduction

Structural and magnetic properties of copper(II) halide salts have long been of interest in the laboratory. Structurally, the coordination geometry of the copper(II) ions has a very diverse range. In addition, the halide ion is an effective bridging ligand, which imposes few steric constraints upon the coordination geometry. These factors provide a mechanism whereby the magnetic superexchange pathways may be systematically varied.[1] Magnetic properties of these salts have proven to be worthwhile in the study of the spin paramagnetism of pseudo-one-dimensional systems, in which the spins on the metal ions interact via superexchange pathways through the halide ions.[2] Magnetostructural correlations for these salts are also of interest due to the effect of the bridging Cu–X–Cu bond angles and coordination geometry on the value of the magnetic coupling constant.[3]

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