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Imidazolium, Nicotinium, and Quinidinium Tetrachlorocuprates(II)

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Imidazolium, nicotinium, and quinidinium tetrachlorocuprate(II) salts have been prepared and characterized spectroscopically. Magnetic susceptibility studies show that nicotinium tetrachlorocuprate exhibits Curie–Weiss behavior all the way down to 1.5 K. Below 4 K quinidinium tetrachlorocuprate(II) shows a slight deviation from the Curie–Weiss law. Remarkably, imidazolium tetrachlorocuprate(II) exhibits magnetic susceptibility behavior consistent with a dimeric formulation of the complex. The complex has a "dimer" electronic transition at 2.52 μm^{-1} which has been interpreted on the basis of molecular orbital calculations. The novel imidazolium complex is formulated as (imidazolium)$_4$Cu$_2$Cl$_8$ and is thought to be stabilized by hydrogen bonding.

Introduction

The tetrachlorocuprate(II) anion, $CuCl_4^{2-}$, is not simple at all. Since a tetrahedral $CuCl_4^{2-}$ anion possesses a $^2T_2$ ground state, the Jahn–Teller effect should be operative and species with lower than T_d symmetry are expected[1] and are observed. The tetrachlorocuprate ion has been found to possess a variety of geometries, e.g., (a) pseudotetrahedral D_{2d} symmetry in Cs_2CuCl_4,[2] (b) planar *and* pseudotetrahedral geometry in $[(CH_3)_2CHNH_3]_2CuCl_4$,[3] (c) 4 + 2 coordination in $[C_6H_5NH_3]_2CuCl_4$,[4] and (d) associated to yield five-coordination in the dimeric anion $Cu_2Cl_8^{4-}$ which can be isolated as the tris(ethylenediamine)cobalt(III) salt.[5] The geometries assumed by the $CuCl_4^{2-}$ ion are summarized in Figure 1, and some representative compounds are given there. The detailed geometry of the pseudotetrahedral $CuCl_4^{2-}$ ion varies remarkably with the cation present.[2,3,6] This behavior in which the *gross* coordination geometry is maintained is an example of distortion isomerism.[7]

The ease with which the $CuCl_4^{2-}$ ion assumes various geometries can be attributed in large part to the operation of the Jahn–Teller effect. Extended-Hückel molecular orbital calculations of the effects of distortions on the $CuCl_4^{2-}$ ion show the presence of broad minima in the total energy vs. distortion parameter curves.[8,9] The effect on the total energy of the free complex anion of distorting the planar (D_{4h}) ion to D_{2d} and T_d geometries is shown in Figure 2. The emergence of broad minima in the results of these calculations indicates that a broad range of geometries may be stabilized by relatively minor interactions such as are involved in crystal-packing forces and hydrogen bonding to cations. Although some progress has been made in this direction, all of the factors which contribute to the geometric preferences of the $CuCl_4^{2-}$ ion have not been determined.

In view of the structural variety exhibited by the $CuCl_4^{2-}$ ion we have undertaken a series of studies of the spectral and magnetic properties of compounds containing this species.[10-12] Herein we report the results of our work with the tetrachlorocuprates of protonated imidazole (ImH^+), nicotine ($NicH_2^{2+}$) and quinidine ($QuinH_2^{2+}$) (see Figure 3). Variable-temperature magnetic susceptibility data reveal that imidazolium tetrachlorocuprate is dimeric while the nicotinium and quinidinium salts are effectively simple paramagnets.

Experimental Section

All chemicals were of the best available reagent or spectroscopic grades. Extreme caution in handling alkaloids, especially nicotine, must be exercised at all times. Care must also be exercised in handling water-soluble salts of alkaloids. C, H, and N analyses were performed by Chemalytics, Inc., Tempe, Ariz. Copper was determined by EDTA titrations.[15]

Preparations of Complexes. Imidazolium, nicotinium, and quinidinium tetrachlorocuprates were prepared by adding stoichiometric quantities of the heterocyclic amine and copper(II) chloride dihydrate to an excess of hot concentrated hydrochloric acid. The reaction mixtures were heated while stirring for several hours and allowed to cool slowly to room temperature. The precipitated products were isolated by filtration and washed with a small amount of concentrated hydrochloric acid, followed by absolute ethanol and diethyl ether. Yields were almost quantitative.

Table I. Electronic and EPR Spectral Data

Compd	ν,[a] μm^{-1}	$g_\parallel$ (±0.005)	$g_\perp$ (±0.005)
$(ImH)_2CuCl_4$	2.52, (0.909), 0.758	2.162	2.066
$(NicH_2)CuCl_4$	0.775	2.140	2.089
$(QuinH_2)CuCl_4$	1.01	2.346	2.104
$[Co(en)_3]_2(Cu_2Cl_8)Cl_2\cdot 2H_2O$	1.08, (1.00)[b]	2.215	2.116
$[Cu(guaninium)Cl_3]_2$[c]	(2.52), 1.01		

[a] Band maxima; shoulders in parentheses. [b] Reference 10. [c] Reference 26.

Anal. Calcd for imidazolium tetrachlorocuprate(II), orange-yellow, $C_6H_{10}N_4CuCl_4$: C, 20.98; H, 2.93; N, 16.31; Cu, 18.50. Found: C, 20.99; H, 2.89; N, 16.35; Cu, 18.48. Calcd for nicotinium tetrachlorocuprate(II), orange, $C_{10}H_{16}N_2CuCl_4$: C, 32.50; H, 4.36; N, 7.58; Cu, 17.19. Found: C, 32.45; H, 4.29; N, 7.54; Cu, 17.13. Calcd for quinidinium tetrachlorocuprate(II), orange-yellow, $C_{20}H_{26}N_2O_2CuCl_4$: C, 45.17; H, 4.93; N, 5.27; Cu, 11.95. Found: C, 45.27; H, 4.93; N, 5.19; Cu, 11.65.

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-3 X-band spectrometer. Quartz 3-mm i.d. tubes were used to hold the samples. Magnetic field, frequency, and field sweep were checked using a sample of vanadyl(IV) acetylacetonate in benzene[16] to which a polycrystalline sample of DPPH free radical (g = 2.0036) was taped. Mull (transmission) electronic spectra were obtained with a Cary Model 17 recording spectrophotometer using a technique described previously.[17]

Magnetic susceptibilities were determined with a Foner vibrating-sample magnetometer[18] operating at a field strength of 10 kG. Calibration of the magnetometer was checked using two standards: $HgCo(NCS)_4$[19] and $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$.[20] The more recent correction to the Weiss constant for $HgCo(NCS)_4$ was applied and both standards agreed within 2% (previously determined[12] to be the upper limit of the uncertainty in our measurements). Temperatures were measured with a GaAs diode which had been standardized against a commercially calibrated diode.[21] A value of 60 × 10^{-6} cgsu was employed for the temperature-independent paramagnetism of the copper(II) ion and the diamagnetic corrections for all of the constituents were made using Pascal's constants.[22]

Results

The EPR spectral parameters of $(ImH)_2CuCl_4$, $(NicH_2)CuCl_4$, $(QuinH_2)CuCl_4$, and $[Co(en)_3]_2(Cu_2Cl_8)Cl_2\cdot 2H_2O$ are summarized in Table I and the EPR spectra are shown in Figures 4 and 5. The EPR spectrum of polycrystalline samples of the pure compounds are all broad, indicative of some dipolar broadening. In no case was metal hyperfine coupling resolved. Only $[Co(en)_3]_2(Cu_2Cl_8)Cl_2\cdot 2H_2O$ shows[10]

Table II. Magnetic Susceptibility Data

Compd	$2J$, cm^{-1}	g^d	$\langle g\rangle^e$	C^f (±1%)	Θ^f (±1%)	Temp range,^{g} K
$(ImH)_2CuCl_4$	-4.04^a	2.15	2.10	0.437	−7.24	10–105
$(NicH_2)CuCl_4$		2.15	2.11	0.433	−0.89	1.5–90
$(Quin\ H_2)CuCl_4$		2.08	2.19	0.406	−2.69	10–50
$[Co(en)_3]_2(Cu_2Cl_8)Cl_2 \cdot 2H_2O$	-14.6^b	2.09	2.15			
$[Cu(guaninium)Cl_3]_2{}^b$	-83^c	2.12				

^{a} Obtained from the Van Vleck equation (see text). ^{b} Reference 11. ^{c} Reference 26. ^{d} Magnetic susceptibility. ^{e} ESR value. ^{f} Obtained from Curie-Weiss fit. ^{g} Temperature range used for the Cure-Weiss fit.

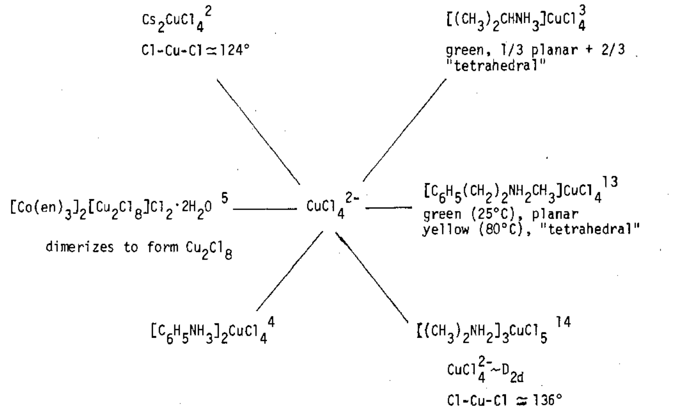

Figure 1. Variety of structures found for the $CuCl_4^{2-}$ species.

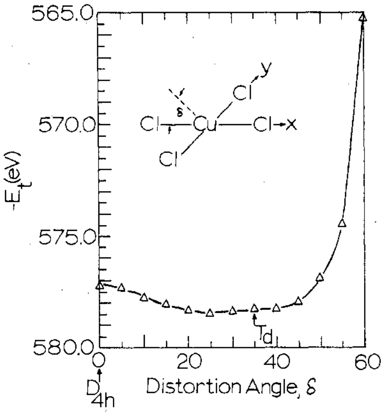

Figure 2. Extended-Hückel total energy ($=\sum_i^{occ} n_i e_i$) vs. the distortion angle δ. (See text.[9]) Starting with a square-planar complex and holding the Cu–Cl bond distances constant, the chloride ions lying on the x axis are raised into the xz plane (by the distortion angle δ) while simultaneously the chloride ions lying on the y axis are moved down by a like amount.

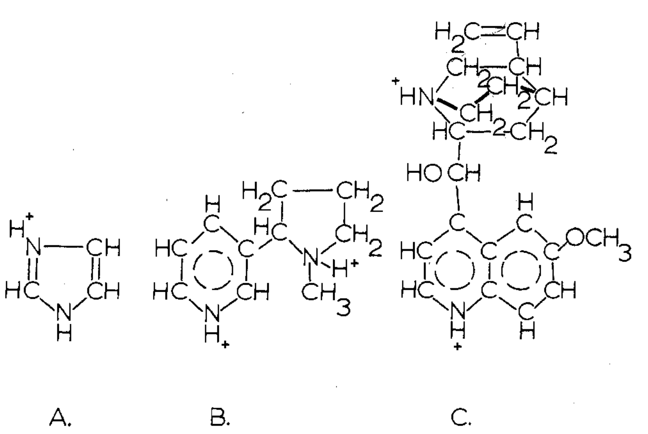

Figure 3. Imidazolium (A), nicotinium (B), and quinidinium (C) cations.

a half-field EPR absorption associated with a $\Delta M_s = \pm 2$ transition. All of the EPR spectra in the region of 3000 G

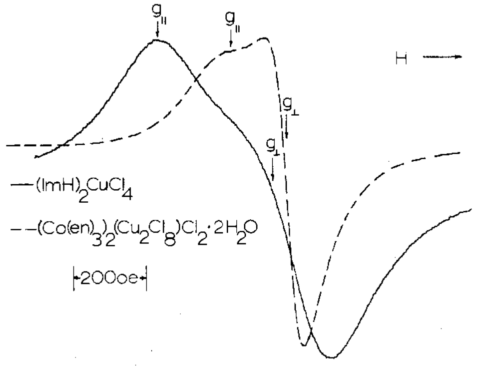

Figure 4. X-Band electron paramagnetic resonance spectra for $(ImH)_2CuCl_4$ and $[Co(en)_3]_2(Cu_2Cl_8)Cl_2 \cdot 2H_2O$ at room temperature.

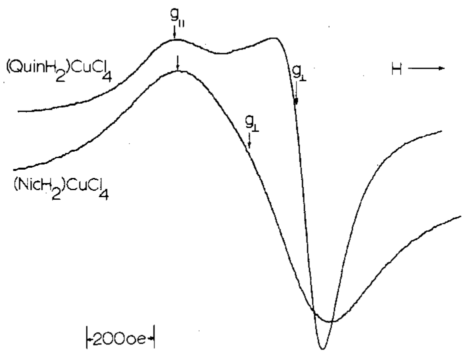

Figure 5. X-Band electron paramagnetic resonance spectra for $(QuinH_2)CuCl_4$ and $(NicH_2)ClCu_4$ at room temperature.

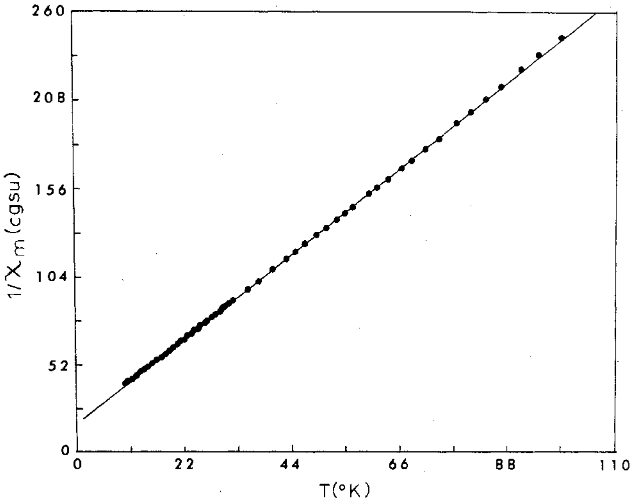

Figure 6. Inverse magnetic susceptibility vs. temperature for $(ImH)_2CuCl_4$. The line represents the best fit to the Curie–Weiss equation.

can be interpreted in terms of an axial spin Hamiltonian. Electronic spectral data are also listed in Table I.

Magnetic susceptibility data are compiled in Table II. The temperature variation of the magnetic susceptibility data of

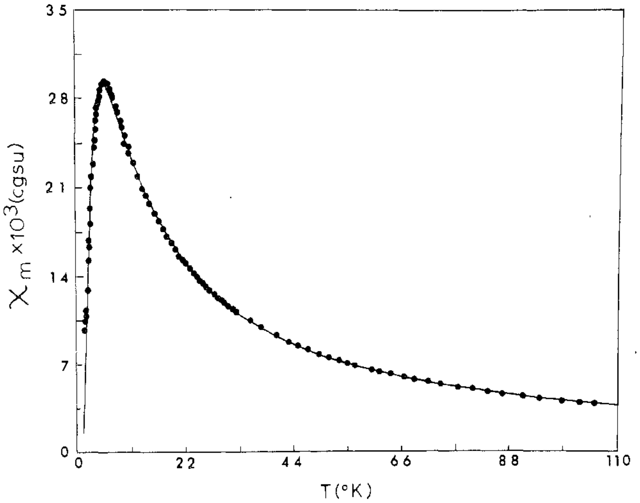

Figure 7. Magnetic susceptibility vs. temperature for $(ImH)_2CuCl_4$. The line represents the best fit to the Van Vleck dimer equation.

all three complexes follow the Curie–Weiss law[23]

$$\chi = \frac{C}{T-\Theta} = \frac{Ng^2\beta^2S(S+1)}{3k(T-\Theta)} \tag{1}$$

where the symbols have their usual meanings, for temperatures above 10 K. Data were fit to the Curie–Weiss law using standard linear least-squares methods. The Curie–Weiss behavior of $(ImH)_2CuCl_4$ is shown in Figure 6. Below 10 K, the magnetic susceptibility of $(NicH_2)CuCl_4$ exhibited Curie–Weiss behavior. Below 4 K the magnetic susceptibility of $(QuinH_2)CuCl_4$ showed a small deviation from Curie–Weiss behavior. The low-temperature magnetic susceptibility data for $(ImH)_2CuCl_4$ are shown in Figure 7. The data can be fit to the Van Vleck dimer equation[23,24]

$$\chi = \frac{Ng^2\beta^2}{3k(T-\Theta')}\left(1 + \frac{1}{3}\exp(-2J/kT)\right)^{-1} \tag{2}$$

The fit of the data to the dimer equation was made using the Simplex function minimization procedure.[25] The best fit was obtained by minimizing the sum of the deviation times the temperature, i.e.

$$R = \sum_i (\chi_i^{\text{calcd}} - \chi_i^{\text{obsd}})^2 T_i^2 \tag{3}$$

The best fit calculated values are $2J = -4.04 \pm 0.2$ cm^{-1}, $g = 2.15 \pm 0.02$, and $\Theta' = -4.68$ K $= -3.52 \pm 0.2$ cm^{-1}. Figure 7 shows the excellent agreement between theory and experiment for $(ImH)_2CuCl_4$.

Discussion

The electronic spectrum of $(NicH_2)CuCl_4$ is in good agreement with that reported by Lamotte-Brasseur.[27] The higher energy of the band maximum in the electronic spectrum of $(QuinH_2)CuCl_4$ shows that it contains a $CuCl_4^{2-}$ ion that is more planar than that found in the nicotinium salt. The trans Cl–Cu–Cl angle, β, in $CuCl_4^{2-}$ complexes may be predicted using the expression[6]

$$\nu\,(\text{cm}^{-1}) = 144.5\beta - 9784 \tag{4}$$

in which ν is the d–d band maximum. Using the spectral data the equation predicts that $\beta = 121°$ for $(NicH_2)CuCl_4$ and 138° for $(QuinH_2)CuCl_4$. In general, the more planar the complex, the higher in energy the band maximum. The electronic spectrum of $(ImH)_2CuCl_4$ will be discussed later.

The magnetic susceptibility data for $(NicH_2)CuCl_4$ and $(QuinH_2)CuCl_4$ show that they are essentially simple $S = {}^1/_2$ paramagnets. The broad EPR spectra can be attributed to dipolar broadening by paramagnetic ions. Magnetic dilution is not achieved by using the bulky nicotinium and quinidinium ions. This suggests that the $CuCl_4^{2-}$ ions are probably less than 8 Å apart in the crystal lattices of $(NicH_2)CuCl_4$ and $(QuinH_2)CuCl_4$. The slight deviation from the Curie–Weiss law seen in the data for $(QuinH_2)CuCl_4$ suggests weak intermolecular interactions and supports this conclusion.

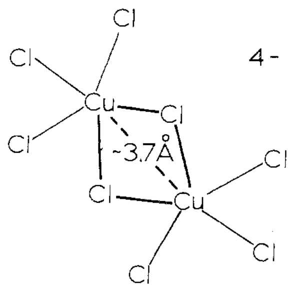

Figure 8. Postulated structure for the anion in $(ImH)_2CuCl_4$. The Cu–Cu separation given is that found in the known $Cu_2Cl_8^{4-}$ ion.[5]

The truly remarkable finding of the present investigation is the dimeric nature of $(ImH)_2CuCl_4$. Colyas et al.[28] have also prepared the compound and, on the basis of Raman spectra, assigned a pseudotetrahedral D_{2d} geometry to the $CuCl_4^{2-}$ ion. Our low-temperature magnetic susceptibility data clearly show that the copper(II) ions are exchange coupled. The excellent fit of the susceptibility data with a dimer model strongly supports a dimeric formulation of the complex. Several dimer formulations must be considered. The compound could contain (a) $Cu_2Cl_8^{4-}$ such as found in the tris(ethylenediamine)cobalt(III) salt,[5] (b) planar $Cu_2Cl_6^{2-}$ as found in $(CH_3)_2NH_2CuCl_3$,[28,29] or (c) nonplanar $Cu_2Cl_6^{2-}$ such as found in Ph_4PCuCl_3[30] and $Ph_4AsCuCl_3$.[31] The magnetic and spectral data suggest that the dimeric species formed by $(ImH)_2CuCl_4$ contains the $Cu_2Cl_8^{2-}$ ion in Figure 8. This supposition will, of course, need to be confirmed by a crystallographic structure determination. Both $(ImH)_2CuCl_4$ and $[Cu(guaninium)Cl_3]_2$, which is structurally similar[26] to $[Co(en)_3]_2(Cu_2Cl_8)Cl_2{\cdot}2H_2O$,[5] exhibit a band at 2.52 μm^{-1} which appears to be characteristic of dimer formation. The characteristic dimer band for $Cu_2Cl_6^{2-}$ species occurs[28,29,31] at about 1.90 μm^{-1}. Unfortunately, meaningful electronic spectral data for $Cu_2Cl_8^{4-}$ could not be obtained for the tris(ethylenediamine)cobalt(III) salt in the 2.5-μm^{-1} region. The $2J$ values for $(ImH)_2CuCl_4$ and $[Co(en)_3]_2(Cu_2Cl_8)Cl_2{\cdot}2H_2O$ are rather close but because of copper–chloride bond length variations as well as changes in the Cu–Cl–Cu bridge angle it is not possible at this time to employ structure–magnetism correlations of the type developed for dimeric hydroxy-bridged copper(II) complexes.[32]

The electronic structure of these compounds have been explored further by performing extended-Hückel molecular orbital (EHMO) calculations for $Cu_2Cl_8^{4-}$. The structural parameters were taken from the crystallographic work of Hodgson et al.[5] The calculations employed the computer program utilized by Hoffmann's group.[33] The parameters employed in the calculations have been discussed in detail elsewhere.[34] The "dimer" bands of dimeric copper(II) complexes have been described in detail elsewhere[35,36] and are best considered to arise from ligand π-orbital to metal-centered excitations. The "dimer" band intensities are generally not very much greater than the metal-localized d–d excitations and, hence, are not likely to arise from excitations of exchange-coupled metal ion pairs,[37] i.e., pairwise excitations.[38] As expected for a large molecule, a large number of energy levels are obtained from the charge-consistent EHMO calculations. The final charges for the copper and bridging chloride ions were 0.44+ and 0.51−, respectively; these values overemphasize the metal–ligand covalency. However, the calculated electronic transition energies for $Cu_2Cl_8^{4-}$ range from 0.55 to 2.4 μm^{-1}. The next range of transition energies is above 10.2 μm^{-1}. Interestingly, the highest reasonable calculated transition energy occurs at 2.381 μm^{-1}. This transition takes place between a molecular orbital level which is primarily composed of chloride p orbitals to a molecular orbital which is predominantly comprised of copper d orbitals. This result strongly suggests, although it certainly does not prove, that the assignment of the 2.5-μm^{-1} dimer band of $Cu_2Cl_8^{4-}$ species is appropriate.

The relatively large value of the Weiss constant, Θ, compared to $2J$ for $(ImH)_2CuCl_4$ is a source of concern. Strictly speaking, the dimer model for the magnetic susceptibility behavior is appropriate only when $\Theta \ll 2J$, i.e., for essentially isolated dimers. Taking this restriction into consideration, several other magnetic models were tested. Attempts to fit the magnetic susceptibility data to linear-chain[39] and two-dimensional[40] Heisenberg models gave broader susceptibility maxima and poorer fits than the one observed. The use of Friedberg's model for pairwise interactions[41] did not yield a good fit of the data. In this model, the Zeeman terms of the triplet level are included along with a molecular field correction, γ, which accounts for small interdimer interactions. Here

$$M = \frac{Ng\beta \sinh(g\beta H/kT)}{\exp(-2J/kT) + 1 + 2\cosh(g\beta H/kT)}$$

with $H = H_0 + \gamma M$. H is the effective field and H_0 is the applied field. The resulting self-consistent equation was used to fit both magnetization and susceptibility. As in the dimer model, γ should be less than $2J$. However, all fits gave $2J = -3.0$ cm^{-1} and $\gamma = -10$, regardless of whether the g value was allowed to vary (the best fit occurred for $g = 2.19$) or was held constant at the EPR value (2.10) or the Curie–Weiss value (2.16). Therefore, the dimer model is the best model for the magnetic susceptibility data for $(ImH)_2CuCl_4$. The rather large value of Θ indicates the presence of additional interactions which are not accounted for in the presently available models. We are led to speculate that hydrogen bonding between the planar imidazolium and $Cu_2Cl_8^{4-}$ ions is in some way responsible for this unusual behavior.

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Registry No. $(ImH)_2CuCl_4$, 61025-88-5; $(NicH_2)CuCl_4$, 61091-23-4; $(QuinH_2)CuCl_4$, 61091-24-5; $[Co(en)_3]_2(Cu_2Cl_8)Cl_2$, 49732-11-8; $(ImH)_4Cu_2Cl_8$, 61025-90-9.

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