shown[21] in an X-ray structure determination of bis(pyridine N-oxide)bis(2,4-pentanedionato)nickel(II) that the nickel atom does not lie in the plane of the pyridine N-oxide ligand molecule; hence, the metal–ligand bond and the ligand π system are not orthogonal. Even if the observed π shifts arose from direct metal–ligand π bonding, it would still be necessary to postulate some unpairing of the paired t_{2g} orbital electrons. Spin–orbit coupling can account for some unpairing, as discussed previously;[19] however, it does not seem fruitful to speculate further on the exact nature of the spin-transfer mechanism in view of the numerous possibilities, of which spin polarization might also be mentioned.[19,22] This last mechanism has been postulated[22] but still awaits documentation.[19,23]

Last, while the observed negative N–CH_3 shifts are consistent with either σ or π spin density in either HBO or LAO, this methyl group exhibits an upfield shift when the pyridine is replaced by a phenyl ring.[4]

Acknowledgments.—We thank the Allied Chemical Co. for support in the form of a fellowship to J. R. H. G. N. L. wishes to acknowledge the hospitality of the Swiss Federal Institute of Technology during the course of this work and thanks the National Science Foundation for a postdoctoral fellowship.

---

(21) W. D. Horrocks, Jr., D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, **7**, 1552 (1968).

(22) D. A. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1960).

(23) H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *Z. Naturforsch.*, **21b**, 809 (1966); M. F. Rettig and R. S. Drago, *Chem. Commun.*, 891 (1966).

DEPARTMENTS OF CHEMISTRY AND PHYSICS,
MONTANA STATE UNIVERSITY, BOZEMAN, MONTANA 59715

On the Preparation and Structure of Acetamidinium Tetrachlorocuprate(II)[1]

BY LEO A. BARES, KENNETH EMERSON, AND JOHN E. DRUMHELLER

Received July 17, 1968

Acetamidinium tetrachlorocuprate has been prepared and characterized. Optical spectra, thermochromism, and epr spectra of this compound are reported and discussed. A structural model is proposed in which $CuCl_4^{2-}$ layers are composed of strips of tetrahedral sites alternated with strips of tetragonal sites. These layers are separated from each other by the acetamidinium ions.

Introduction

As part of a program of investigating ligands similar in geometry to acetate ion, the coordination chemistry of acetamidine and some of its derivatives is under study. During this study a number of new chlorometalate salts have been prepared; this paper reports the investigations on one of these, acetamidinium tetrachlorocuprate(II), $[CH_3C(NH_2)_2]_2CuCl_4$.

Copper forms a great many double salts with other chlorides, and these display various structural forms. X-Ray crystal structures have been reported on a number of these[2,3] and considerable literature is available on spectra and magnetic properties of the various structural types.

A brief review of the structural variations which have been observed in tetrachlorocuprates may be useful. Cs_2CuCl_4 is an orange compound, which contains discrete distorted tetrahedral $CuCl_4^{2-}$ groups.[2,3a] Two tetraalkylammonium tetrachlorocuprates have also been investigated crystallographically and found to contain discrete, distorted tetrahedral $CuCl_4^{2-}$ ions.[3] In contrast, the large number of known monoalkylammonium tetrachlorocuprates[4] have a different structure in which the copper is coordinated in square-planar geometry to four chloride ions and exhibits weak bonding to two more chlorides in other $CuCl_4^{2-}$ groups.[5] The geometry of the copper site in these structures is the usual tetragonally distorted octahedron which has become so familiar.

The monoalkylammonium tetrachlorocuprates also exhibit thermochromism, a property which Cs_2CuCl_4 and $(R_4N)_2CuCl_4$ do not share. In particular, all of the monoalkylammonium salts which have been studied transform from yellow to green at low temperatures. The temperature of the transition varies with the alkyl group. In isopropylammonium tetrachlorocuprate it is above room temperature. The structure of the low-temperature green form has not yet been determined.

$[CH_3C(NH_2)_2]_2CuCl_4$ is bright yellow and thermochromic, and very large crystals can easily be prepared. It was felt that the structure could probably be easily deduced from its properties in the midst of this wealth of data. The results of this study have been both interesting and unexpected.

Experimental Section

Sample Preparation.—$[CH_3C(NH_2)_2]_2CuCl_4$ was prepared by mixing stoichiometric amounts of acetamidine hydrochloride and anhydrous copper(II) chloride in ethanol. This is the same procedure used by Remy and Laves[4] to prepare alkylammonium

---

[1] Taken in part from the Master's Thesis of L. A. B., presented and accepted at Montana State University, Dec 1965. Work supported by the National Science Foundation.

(2) L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

(3) (a) B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961); (b) M. Bonamico and G. Dessy, *Acta Cryst.*, **A21**, 136 (1966).

(4) H. Remy and G. Laves, *Ber.*, **66**, 401 (1933).

(5) R. D. Willett, *J. Chem. Phys.*, **41**, 2243 (1964).

tetrachlorocuprates; this salt is, however, more soluble than theirs and does not precipitate on mixing. Precipitation can be induced by addition of diethyl ether. In order to grow large crystals, ethanol solutions were placed in a desiccator over diethyl ether, and the ether was allowed to condense slowly into the solution. The compound crystallizes as long, thin rectangular plates with a deep yellow color.

Physical Measurements.—Electronic spectra were recorded on a Beckman DK-2 spectrophotometer and vibrational spectra were taken on a Beckman IR-4 infrared spectrometer. The wavelength scan of the latter was checked at intervals using a piece of styrene film as a standard. The electron paramagnetic resonance (epr) measurements were begun at 9.5 GHz (X band) but were continued at 24.0 GHz (K band) for reasons that are apparent below. Both spectrometers used standard detection techniques and cylindrical cavities operating in a TE_{011} or similar modes. The crystal mounting was designed so that the sample could be rotated in two orthogonal planes; the crystal was mounted so that these planes of rotation corresponded roughly to two Miller planes of the crystal.

Results and Discussion

The infrared spectrum of the powdered solid in a KBr pellet is identical with the spectrum of acetamidine hydrochloride, indicating that the acetamidinium ion is the organic species present. This similarity also suggests that the nitrogen atoms of the acetamidinium ion are not coordinated in any way to the copper atoms. Since the compound could be grown as extremely thin crystals, an optical spectrum was taken in an effort to determine the copper coordination geometry. This could only be taken perpendicular to the plane of the crystals, and in this direction the spectrum was unpolarized. The spectrum obtained is shown in Figure 1 and is quite different from that reported by Willett[6] for methyl- and ethylammonium tetrachlorocuprates. The spectrum of ethylammonium tetrachlorocuprate was also taken for comparison, and a sample of this is reproduced in Figure 1. The difference between these two spectra is surprising, because it was felt that since acetamidinium tetrachlorocuprate was thermochromic it was probably very similar in structure to the monoalkylammonium salts, whereas, in fact, the spectrum of acetamidinium tetrachlorocuprate is very similar to that reported by Ferguson[7] for Cs_2CuCl_4 in which the $CuCl_4^{2-}$ are discrete distorted tetrahedra.

Thus, the optical data suggest a tetrahedral coordination sphere, while the thermochromism obviously indicates a tetragonal geometry. Neither of these observations represents hard evidence. An attempt was made to resolve this conflict with an epr experiment.

The epr spectrum of tetrahedral $CuCl_4^{2-}$ had been reported in detail by Sharnoff,[8] and Willett[6] had recently studied the epr spectrum of methylammonium tetrachlorocuprate. The epr spectra for these two different coordination geometries are quite distinct. The values for $g_{\|}$ and $g_{\perp}$ are significantly different, as shown in Table I. Furthermore, in the tetragonal geometry the observed line is Lorentzian in shape and appears to be exchange narrowed because of the presence of chloride bridges between adjacent copper atoms.

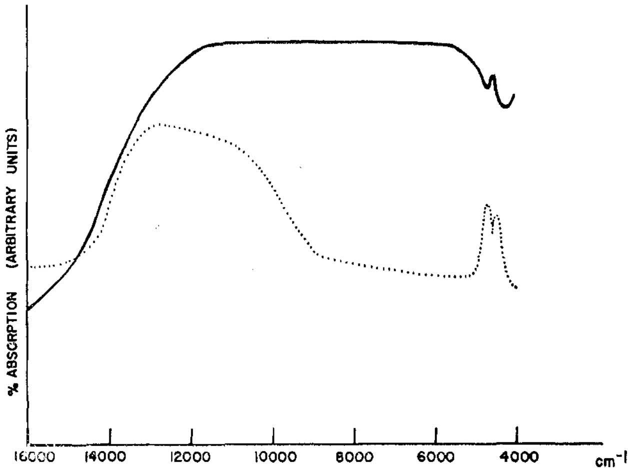


Figure 1.—Spectra of tetrachlorocuprates: $(CH_3NH_3)_2CuCl_4$, · · · ·; $[CH_3C(NH_2)_2]_2CuCl_4$, ———.

Table I

g Values for Tetrahedral and Tetragonal Cu Sites

Compd	$g_{\|}$	$g_{\perp}$	Cu site symmetry	Ref
$(CH_3NH_3)_2CuCl_4$	2.238	2.046	D_{4h}	6
Cs_2CuCl_4	2.384	2.094	D_{2d}	8

The quotation of $g_{\|}$ and $g_{\perp}$ in this way masks some of the experimental details. For the tetragonal system $g_{\|}$ cannot be obtained directly because alternate $CuCl_4^{2-}$ groups have their tetragonal axes at right angles to each other. A value for $g_{\perp}$ can be obtained by orienting *H* perpendicular to the $CuCl_4^{2-}$ layer. Experimentally this requires orienting the crystal so that the magnetic field, *H*, is perpendicular to the well-developed face. When *H* is parallel to the principal face of the crystal, a maximum value of *g* is obtained and the relation

$$g_{max} = {}^{1}/_{2}(g_{\|} + g_{\perp})$$

can be used to calculate $g_{\|}$. An analogous procedure was used by Sharnoff[8a] to calculate $g_{\|}$ and $g_{\perp}$ for Cs_2CuCl_4.

On the other hand, the epr spectrum of $[CH_3C(NH_2)_2]_2CuCl_4$ at X band gave g_{max} when *H* was oriented perpendicular to the well-developed crystal face instead of g_{min}, while g_{min} was obtained when *H* was parallel to this face. The line shape was almost Lorentzian, but there was an angularly dependent distortion to the line which suggested the possibility of a second line in the spectrum with a different principal axis to the *g* tensor.

The K-band spectrum, in fact, confirmed this by resolving the two lines. Figure 2 shows a sample of the X-band data and also shows a theoretical Lorentzian line. This datum was taken as an absorption spectrum to observe more clearly the departure from a Lorentzian line. Figure 3 shows a sample of the K-band data taken as the first derivative of the absorption spectrum. The experimental curve can be duplicated

---

(6) R. D. Willett, O. L. Liles, Jr., and C. Michelson, *Inorg. Chem.*, **6**, 1885 (1967).

(7) J. Ferguson, *J. Chem. Phys.*, **40**, 3406 (1964).

(8) (a) M. Sharnoff, *ibid.*, **41**, 2203 (1964); (b) *ibid.*, **42**, 3383 (1965).

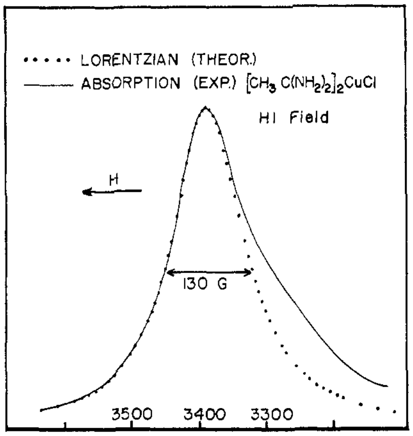


Figure 2.—Comparison of theoretical and observed epr spectra of $[CH_3C(NH_2)_2]_2CuCl_4$ at 9.5 GHz.

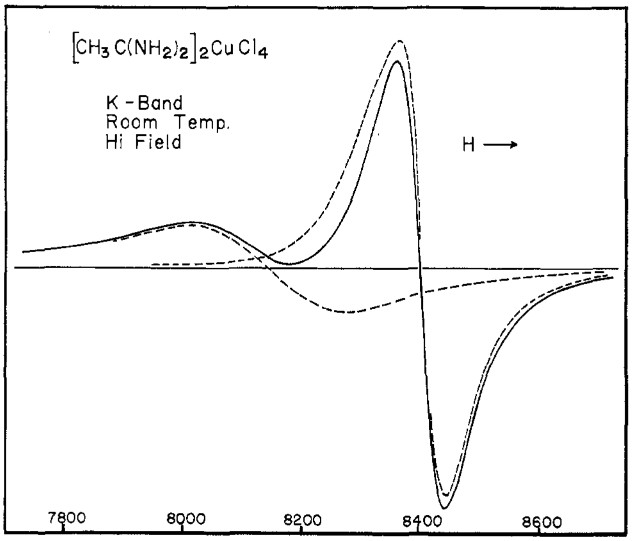


Figure 3.—Sample derivative epr spectrum of $[CH_3C(NH_2)_2]_2CuCl_4$ at 24 GHz showing a tracing of the actual data as the solid line and how it can be fitted by summing the derivatives of a wide Gaussian and a narrow Lorentzian line both shown as dashed lines.

by the addition of two derivative curves having line widths of about 265 and 135 G and separated by about 250 G. This separation occurs near $g_{\min}$ for the intense line. The g values calculated from these two lines at K band are given in Table II. From this it would appear that these represent two magnetically different sites of the copper atoms in the crystal with one site showing the expected exchange narrowing and the other showing only dipolar broadening. The integrated intensities of these lines can be seen to be approximately equal.

TABLE II

g VALUES FOR TWO Cu SITES IN $[CH_3C(NH_2)_2]_2CuCl_4$

Type of site	$g_{\parallel} = g_{\max}$	$g_{\perp} = g_{\min}$
Exchanging	2.337 ± 0.002	2.061 ± 0.002
Isolated	2.355 ± 0.004	2.063 ± 0.004

In addition, the magnetic axes of these two sites make an angle of about 23° with each other and these axes (Z axes) are both in a plane perpendicular to the long axis of the crystal as can be seen in Figure 4. The maximum g for both lines is observed with H approximately perpendicular to the well-developed face, while the minimum in g occurs with H nearly parallel to this face.

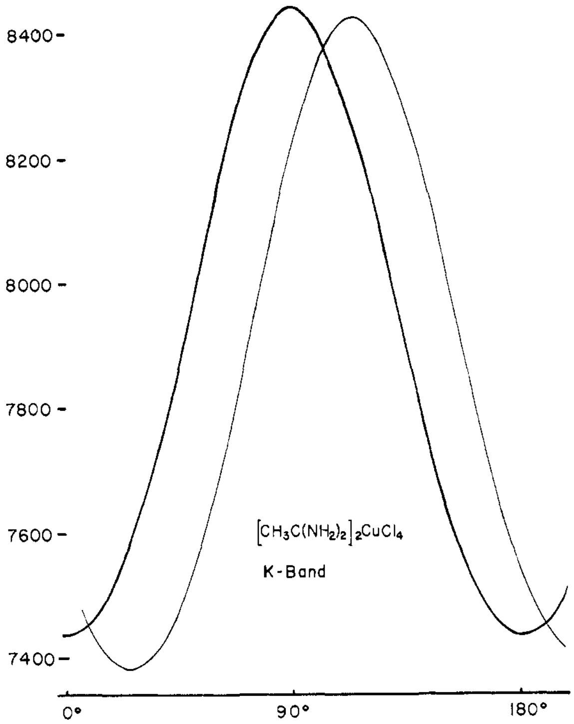


Figure 4.—Field in gauss *vs.* the angle about the needle axis for the two lines in $[CH_3C(NH_2)_2]_2CuCl_4$.

The similarity of the g values of the second site to those reported by Sharnoff for Cs_2CuCl_4, as well as the fact that there appears to be no exchange narrowing for copper resonances in the tetrahedral site of Cs_2CuCl_4,[8a] strongly suggests that the second site is a tetrahedral $CuCl_4^{2-}$ site. The observed absorption spectrum of the crystals could be readily explained as a superposition of tetrahedral and tetragonal spectra. However, the observed g values for the exchange site differ considerably from those obtained by Willett for a known tetragonal site, and this difference is still unresolved.

The following structural model explains these observations. The structures of $(CH_3NH_3)_2CuCl_4$ and Cs_2CuCl_4 were examined and it was discovered that some interesting similarities in the arrangement of chloride ions occur in the two cases. Idealized representations of these two structures are shown in Figure 5. The cations have been omitted from these drawings, the copper ions occupy either octahedral or tetrahedral holes, depending on the structure, and the alkali or amine cations act as "separators" between these layers of chloride ions. Structure a has only octahedral holes in the close packed lattice, and structure b has only tetrahedral; the structures can be interconverted by moving one-fourth of all chlorides to an adjacent site.

The marked similarity of these two structures seemed to indicate that there might indeed be a way of combining them in a single structure. The immediate and obvious answer was that alternate layers of tetrahedral and octahedral sites might exist. This would require,

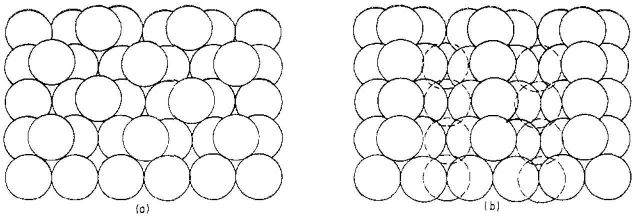


Figure 5.—Chloride-packing models of the $CuCl_4$ layers in (a) $(CH_3NH_3)_2CuCl_4$ and (b) Cs_2CuCl_4.

however, that the magnetic axes of the two sites coincide, contrary to observation.

Further study of these models yielded a structure which adequately explains all of the observations. An examination of the tetrahedral packing of Cs_2CuCl_4 (Figure 5b) reveals that the structure can be thought of as a series of rows of isolated $CuCl_4^{2-}$ ions, the rows being alternately "up" or "down" with reference to the principal layer of chloride ions. Figure 5b shows the main layer of chloride ions, and the rows of ions which are above this main layer. Between these rows and below the main layer in the diagram are two additional rows of tetrahedra; the chloride ions below the main layer which belong to these rows are shown as dotted circles.

The structure of $(CH_3NH_3)_2CuCl_4$ in Figure 5a can be similarly decomposed into a series of rows of square-planar $CuCl_4^{2-}$ units held together by weak Cu–Cl bonds. In these hypothetical rows the coordination of the copper is tetragonal pyramidal, and the sixth site of the distorted octahedral coordination is filled if the rows are brought together to form the layer structure. If the rows constructed from Figure 5a are laid next to those constructed from Figure 5b, they fit together neatly to form layers of alternately tetrahedral and octahedral sites. In order to make the populations of the two sites equal as required by the epr intensities, there must be two tetrahedral rows, one "up" and one "down." The model can easily be built exactly planar, which would make the principal magnetic axes coincident.

However, if this layer bends a little at each line where differing structures join to give a pleated layer, it would account for the differences in orientation of the two sites. This might easily be caused by chloride–chloride repulsions along the joining line.

This suggests in turn some predictions about the space group and unit cell of this compound, compared to $(C_2H_5NH_3)_2CuCl_4$, which has about the same-size cation and should therefore have similar dimensions. First, one cell dimension of the three should be doubled, because of the alternate types of structure; second, the symmetry should be lowered. The cell dimensions of $[CH_3C(NH_2)_2]_2CuCl_4$ have been determined by Witters[9] and are compared to those of $(C_2H_5NH_3)_2CuCl_4$ in Table III.

Table III

Unit Cell Parameters of Ethylammonium and Acetamidinium Tetrachlorocuprate

Compd	a, Å	b, Å	c, Å	β, deg	Space group
$(C_2H_5NH_3)_2CuCl_4$	21.18	7.47	7.35	...	Pbca
$[CH_3C(NH_2)_2]_2CuCl_4$	23.06	7.93	14.69	94.5	$P2_1/a$

The dimension in which the doubling occurs corresponds to the direction in which the misalignment of the magnetic axes of the two sites is observed.

There still remains the problem that, for the exchange site, the observations of $g_{\max}$ and $g_{\min}$ indicate that the axis of distortion of the tetragonal coordination is perpendicular to the chloride layer, rather than parallel to it. The idealized octahedral symmetry of the copper ions in Figure 5a includes a fourfold axis perpendicular to the chloride layer along which distortion could occur. This is a perfectly acceptable model, but there seems to be no adequate explanation for the shift of axes in this manner. There is one experimental datum which argues against it: this structure should actually shorten the b axis slightly relative to $(C_2H_5NH_3)_2CuCl_4$, whereas b is in fact longer for this compound.

There remains one other problem which we cannot satisfactorily explain. Each tetrahedral chlorocuprate ion shares one of its chloride ions with a square-planar chlorocuprate ion, thereby completing the octahedral coordination. This chloride ion thus forms a bridge between tetrahedral and square-planar copper ions through which exchange might be expected to occur. The experimental evidence seems to indicate that such exchange does not occur, but speculations about why do not seem profitable at this stage.

One way of avoiding this difficulty would be to distort the octahedral sites to trigonal-bipyramidal sites; this would remove the chloride bridges from the tetrahedral sites but leave bridges between adjacent trigonal-bipyramidal sites. However, for trigonal symmetry, $g_{\|}$ must equal the free-electron g value.[10] Since this is clearly not the case, this possibility has been omitted from the discussion.

There exist a very large number of other structural possibilities which might be considered. However, the presence of thermochromism and the similarity in cell dimensions to those of $(C_2H_5NH_3)_2CuCl_4$ suggest strongly that these two structures are quite similar. Consideration has therefore been limited to structures which could be derived from the known structure of $(C_2H_5NH_3)_2CuCl_4$. For example, the possibility of structures in which the chlorocuprate layer exhibits a stoichiometry different from $CuCl_4$ have been omitted on this basis.

Summary

The preparation, optical spectra, thermochromism, and epr spectrum of $[CH_3C(NH_2)_2]_2CuCl_4$ have been described and compared to the properties of other tetrachlorocuprates of known structure. On the basis

---

(9) R. D. Witters, private communication, 1967. A complete X-ray analysis of this structure is in progress.

(10) See, for example, W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).

of these observations, a consistent structural model for this compound has been proposed.

Acknowledgments.—The authors are grateful for National Science Foundation support from several different grants at various stages of this research. L. A. B. is indebted to the Department of Health, Education, and Welfare for an NDEA Fellowship from 1962 to 1965. They also thank Paul H. Amundson for help with some of the data.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

Multidentate Ligand Kinetics. XIII. Lead(II) and Copper(II) Suppression of Their Rate of Exchange with 1,2-Diaminocyclohexanetetraacetatocadmate(II)

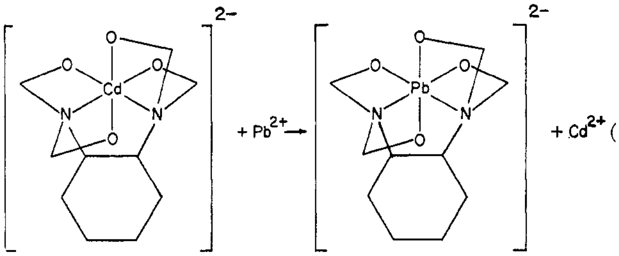
BY GREGORY F. SMITH AND DALE W. MARGERUM[1]

Received June 3, 1968

The rate of Pb(II) substitution of Cd(II) in $CdCyDTA^{2-}$ (CyDTA is *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate) decreases as the concentration of Pb(II) increases. This is an example of an exchange reaction in which a reactant suppresses its own rate of exchange. The anomaly results from the steric requirements of CyDTA which prevent the direct exchange of metal ions. Instead the exchange rate is controlled by a hydrogen ion reaction with $CdCyDTA^{2-}$. Lead(II) forms weak complexes with the acetate groups of $CdCyDTA^{2-}$ and these complexes block the hydrogen ion reaction. Hence excess Pb^{2+} slows the rate of appearance of $PbCyDTA^{2-}$. Copper behaves in a similar manner.

Introduction

As in the exchange reactions of other metal–CyDTA complexes,[2,3] there is no direct metal ion attack on the cadmium–CyDTA complex and the rate of the reaction in eq 1 does not increase with the lead ion concentration. Sterically it is not possible to bind both cadmium and lead to the two nitrogen atoms of CyDTA. As a result the most important kinetic path is hydrogen ion displacement of cadmium followed by reaction with lead. However, unlike the previously studied metal–CyDTA exchange systems the rate of formation of product is suppressed by excess concentrations of the exchanging metal ion. Thus the rate of appearance of $Pb(CyDTA)^{2-}$ in eq 1 is decreased by increasing concentrations of lead. The cadmium–CyDTA reaction with copper also becomes slower as the copper concentration increases. In both cases a first-order dependence in hydrogen ion concentration is observed as in all other metal–CyDTA exchange reactions.[2] Suppression of the reaction rate by an excess of the scavenger ion (Pb^{2+} or Cu^{2+}) is attributed to the formation of weak complexes between the scavenger ion and the cadmium–CyDTA complex. Species such as $CdCyDTA^{2-}$–Pb^{2+} are not readily attacked by hydrogen ion. A similar mechanism (eq 2) is proposed when copper ion is the scavenger. As a result, the higher the concentrations of the exchanging metal ion (Pb^{2+} or Cu^{2+}), the slower is the exchange reaction.



(1)

$$\begin{tikzcd}
CdCyDTA^{2-} \arrow[d, shift right, "Pb^{2+}"'] & + H^+ \arrow[r, shift left, "k_H^{CdCy}(rds)"] & HCyDTA^{3-} + Cd^{2+} \arrow[l, shift left] \arrow[d, "+Pb^+"', "-H^+", "rapid"] \\
Cd(CyDTA)Pb \arrow[u, shift right] \arrow[d, shift right, "Pb^{2+}"'] & & PbCyDTA^{2-} \\
Cd(CyDTA)Pb_2^{2\bullet} \arrow[u, shift right] & &
\end{tikzcd} \quad (2)$$

$\left.\begin{matrix}Cd(CyDTA)Pb\\Cd(CyDTA)Pb_2^{2\bullet}\end{matrix}\right\}$ no reaction with H^+

Experimental Section

Solutions of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ were standardized by complexometric titrations with CyDTA or EDTA. The acid form of CyDTA (LaMont Laboratories) was dissolved in NaOH and standardized with copper using Chrome Azurol S indicator. Cadmium–CyDTA solutions were prepared with about 10% excess CyDTA. The ionic strength was controlled at 0.10 *M* using KNO_3. All reactions were at 25.0 ± 0.1°.

The reactions between $CdCyDTA^{2-}$ and Pb^{2+} were followed by measuring the absorbance of $PbCyDTA^{2-}$ at 260 mμ with a Cary 16 spectrophotometer. The molar absorptivities ($cm^{-1}M^{-1}$) of the species in solution were 1860 for $PbCyDTA^{2-}$, 20 for $CdCyDTA^{2-}$, 3.0 for $Pb(C_2H_3O_2)_n^{2-n}$, 1.5 for NO_3^-, and 1.0 for $C_2H_3O_2^-$. The reactions with copper were followed at 310 mμ ($\epsilon_{CuCyDTA}$ 1099) and 700 mμ ($\epsilon_{CuCyDTA}$ 111). Most reactions were measured to constant absorbance (A_∞) or for more than 2 half-lives. Excellent first-order plots were observed from log ($A_\infty - A$) against time in accord with the rate expression

$$\frac{d[PbCyDTA^{2-}]}{dt} = -\frac{d[CdCyDTA]}{dt} = k_0[Cd(CyDTA)_T] \quad (3)$$

---

[1] Correspondence to be addressed to this author.

[2] D. W. Margerum, P. J. Menardi, and D. L. Janes, *Inorg. Chem.*, **6**, 283 (1967).

[3] D. W. Margerum and T. J. Bydalek, *ibid.*, **2**, 683 (1963).