spectra (Figure 2B), which seem symmetrical, are taken to represent widely split A + E offspring of the $T_{1g}(O_h)$ upper level, only one derivative point group will furnish the correct selection rule, namely, C_3. This would be consistent with expectation for the tris(amino acid) complex of the β or cis configuration.[17] However, one might consider the spectrum to represent a three-component spectrum with one component forbidden, which would match C_{2v} symmetry, which might correspond to one form of cis bis complex. There is an obvious difficulty, looking at the peaks, of matching the two components of the CD to yield the observed absorption curve. Synthesis of the absorption peak from Gaussian components in fact shows the major absorption component to be a third one at about 603 nm, which has no CD associated, and is about as intense as the 540- and 665-nm absorption components taken together.

If this spectrum actually is that of the cis complex and if the spectrum seen in the pH 4–6 region, independent of ligand ratios from 0.5–5:1, is reasonably to be attributed to the 1:1 complex, what represents the trans 2:1 complex, expected from the analogous crystalline material[7] already discussed? This would need be the variant seen between pH 6 and 8, for both 1:1 and 2:1 ligand–Ni(II) systems, which has a single, positive component in the red, at 595 nm (Figure 2D). In the 400-nm region it differs from the 1:1 spectrum only in small relative intensity alterations between the components. An awkwardness for this assignment is the fact that near pH 6 the intensity of the 595-nm peak is almost precisely the same for a solution with a 1:1 ligand–nickel(II) ratio, for which at most half the Ni(II) can appear as 2:1 complex, as for the solution with a 5:1 ligand ratio. Potential support for the assignment is the single CD peak, as for the mixed trans complex, and that the spectrum as a whole is closely the sign inverse of the CD spectrum assigned to a 2:1 species for the complexes with the aliphatic amino acids (see Figure 1f–1h, ref 2).

Whether the high-pH complex is the cis bis chelate, which seems most probable, or possibly tris chelate (which would be derived from such a precursor), the factors that may influence the formation of cis rather than trans bis chelate are obviously of interest. The best clue may be the fact that even with 5:1 ligand–nickel(II) solutions, alkaline pH seems to be required to transform the intermediate spectrum (with a single peak in the red), which seems to characterize trans bis chelate, into the form which is probably cis bis chelate. One hypothetical scenario might start with the bis-aquo trans bis chelate, in which action of the elevated pH transforms an axial water group into an hydroxyl. One of the amino acid moieties, or merely its amino group, now dissociates in kinetic equilibrium. At pH 7–8, say, well below its pK_H, the amino group protonates. Let us assume that now RNH_3^+ attacks NiOH (with formation of product H_2O) in preference to $NiOH_2$ (with formation of H_3O^+). Since the position thus attacked is axial to the original plane, the chelation is now cis, and the change is made. Possibly also involved may be a difference in the electrostatics of RNH_3^+ at the lower pH and RNH_2 at pH sufficiently elevated to partially dissociate the former, but both mechanisms could operate, in proportion appropriate to the pH.

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[17] B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965), and references cited therein.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Chelative Addition of Hydrazine to Coordinated Isocyanides. The Structure of 1,1′-Dichloropallado-2,5-di(methylamino)-3,4-diazacyclopentadiene, $[(CH_3)_2C_2N_4H_4]PdCl_2$

BY WILLIAM M. BUTLER AND JOHN H. ENEMARK*

Received April 13, 1971

The structure of the addition product of hydrazine with *cis*-dichlorobis(methyl isocyanide)palladium has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the space group D_{2h}^{17}-*Cmcm* with four molecules in a cell of dimensions a = 18.043 (4), b = 7.326 (1), and c = 6.839 (1) Å. The observed and calculated densities are 2.141 (7) and 2.141 g cm^{-3}, respectively. Full-matrix least-squares refinement of the structure has resulted in $R = 0.030$ for the 599 data having $F_o^2 > 3\sigma(F_o^2)$. The Pd atom is four-coordinate and bonded to two Cl atoms and to the two C atoms of the novel –C–N–N–C– chelate skeleton resulting from the addition of a hydrazine molecule to two coordinated isocyanide molecules. The complex is rigorously planar and is required to have *mm*-C_{2v} symmetry. The Pd–Cl distance is 2.387 (1) Å and the Pd–C distance is 1.948 (5) Å. The distances within the chelate ring are C–N = 1.309 (6) and N–N = 1.395 (8) Å. The molecular plane of the complex is normal to the c axis of the crystal, and the molecules are stacked to form chains parallel to c.

Introduction

Reactions between tetrakis(methyl isocyanide)platinum(II) and hydrazine were first reported by Chugaev and coworkers[1] in 1925. They isolated a red compound which they formulated as **1** on the basis of conductivity and analytical data. Treatment of **1** with hydrochloric acid resulted in the evolution of methyl isocyanide and

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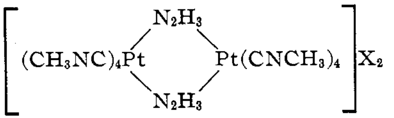
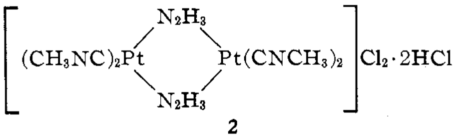
[1] L. Chugaev, M. Skanavy-Grigorieva, and A. Posniak, *Z. Anorg. Allg. Chem.*, **148**, 37 (1925).

the formation of yellow crystals ascribed structure 2.



1, $X^- = Cl^-, I^-, ClO_4^-, N_3^-$



2

The renewed interest in the chemistry of isocyanide complexes of transition metals in recent years has led to a reinvestigation of 1 and 2. Although originally formulated as containing coordinated isocyanide, compound 2 did not show a CN stretching frequency characteristic of coordinated isocyanide.[2] This suggested that the coordinated isocyanide ligand had reacted with the hydrazine to yield a new ligand. Indeed, reactions of coordinated isocyanide ligands have been previously reported.[3-8]

In order to elucidate the nature of the hydrazine–isocyanide reaction and to understand the relationship between the red and yellow compounds, X-ray structure determinations of these complexes have been undertaken. We report here the structure of the Pd analog of 2, $[(CH_3)_2C_2N_4H_4]PdCl_2$. Our results show that structure 2 is not correct. The compound is actually monomeric and contains a novel chelating ligand. A preliminary account of this work has appeared.[2]

Experimental Section

A sample of the compound $[(CH_3)_2C_2N_4H_4]PdCl_2$ in the form of very fine yellow needles was kindly supplied by Professor A. L. Balch. The preliminary structure determination[2] from 188 photographic data obtained from a small crystal clearly revealed the geometry of the complex but did not distinguish between C and N atoms with certainty or locate the hydrogen atoms.

Suitable single crystals for obtaining intensity data by counter techniques were grown with difficulty from 1.2% aqueous HCl by slowly cooling the solution from 80°. The crystals formed as needlelike hexagonal prisms with *c* being the long axis of the crystal. Preliminary precession photographs (Cu Kα) confirmed that the crystals were orthorhombic with the diffraction conditions hkl, $h + k = 2n$ and $h0l$, $l = 2n$. These conditions are consistent with the space groups D_{2h}^{17}-$Cmcm$, C_{2v}^{12}-$Cmc2_1$, or C_{2v}^{12}-$C2cm$ (alternative setting of $Ama2$). The centrosymmetric space group $Cmcm$ was assumed and verified by successful solution and refinement of the structure (*vide infra*).

A number of crystals of visually good quality showed large splittings when examined by an ω scan on a Picker FACS-I four-circle diffractometer at a takeoff angle of ~0.7°. Eventually a crystal was found in which the satellite peak was less than 50% of the intensity of the main peak and in which the total width of the two peaks at half-height was less than 0.2°. The approximate dimensions of the crystal were 0.09 × 0.09 × 0.11 mm, and the *c* axis was approximately collinear with the ϕ axis of the diffractometer. Nine reflections in diverse regions of reciprocal space with 2θ in the range 26–34° were carefully centered on the Mo Kα_1 peak (λ 0.70930 Å). An ω scan was done for each of the reflections to ensure that the mosaicity fell within the limits described above. A least-squares refinement of the setting angles for the nine reflections gave unit cell parameters at 23 ± 2° of $a = 18.043$ (4), $b = 7.326$ (1), and $c = 6.839$ (1) Å. The density of the crystals was determined to be 2.141 (7) g cm^{-3} by the gradient column technique. This is in excellent agreement with 2.141 g cm^{-3} calculated for four molecules of $[(CH_3)_2C_2N_4H_4]PdCl_2$ per unit cell.

An incident beam monochromator equipped with a graphite crystal was used to obtain Mo Kα radiation. The θ–2θ axis of the monochromator was perpendicular to the θ–2θ axis of the diffractometer. Data were collected using the θ–2θ scan technique and an asymmetric scan range from 2θ (Mo Kα_1) −0.85° to 2θ (Mo Kα_2) +0.85° at a takeoff angle of 1.5°. The pulse height analyzer was set to admit ~90% of the Mo Kα peak and the scintillation counter was 24 cm from the crystal. Cu foils with attenuation factors of ~1.7 were inserted into the diffracted beam whenever the count rate exceeded ~10^3 counts sec^{-1}. During data collection the intensities of three reflections were monitored every 50 reflections. None of the standard reflections showed any systematic changes in intensity during the data collection. The maximum variation of any standard from its mean value was 3.7%. A total of 737 reflections having $2\theta \leq 60°$ were obtained. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.[9-11] The polarization correction used was $P = 0.5(\cos^2 2\theta_m + \cos^2 2\theta)$ where θ_m is the Bragg angle of the monochromator crystal and θ is the Bragg angle of the observed reflection. Standard deviations were assigned to the corrected intensities by the formula

$$\sigma(F^2) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pF^2)^2]^{1/2}$$

where CT is the total integrated peak count obtained in time t_c and B_1 and B_2 are the background counts each obtained in time t_b. F^2 is the corrected intensity and p was taken as 0.04.

The absorption coefficient for the compound for Mo Kα radiation is 23.2 cm^{-1}. The faces of the crystal were identified as {100}, {110}, {1$\bar{1}$0}, and {001}, and the crystal was carefully measured. Sample calculations on several reflections showed that the absorption correction only ranged from 1.11 to 1.12 and that no correction was necessary.

Solution and Refinement

Position of the Pd and Cl atoms were readily deduced from a Patterson function computed from the photographic data, and a difference electron density map revealed the remaining nonhydrogen atoms. The final atomic positions from the photographic investigation were used as starting parameters for the refinement of the diffractometer data. This refinement was based upon F_o, with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. The weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Pd were from Cromer and Waber;[12] the factors for Cl, C, and N were from the usual tabulation.[13] Hydrogen scattering factors were those calculated by Stewart, *et al.*[14]

The effects of anomalous dispersion were included in F_c;[15] the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer[16] were used for Pd and Cl. The initial structure factor calculation for the diffractometer data gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.216$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.241$ for the 599 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Two cycles of refinement with anisotropic thermal parameters assumed for the Pd atom and isotropic thermal parameters assumed for all other atoms reduced the agreement factors to $R_1 = 0.062$ and $R_2 = 0.079$. Two cycles with

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[2] A. Burke, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, **92**, 2555 (1970).

[3] P. M. Treichel and J. P. Stenson, *Inorg. Chem.*, **8**, 2563 (1969).

[4] P. M. Treichel and J. P. Stenson, *Chem. Commun.*, 423 (1969).

[5] E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *ibid.*, 1322 (1969).

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[7] Y. Yamamoto, H. Yamazaki, and N. Hagihara, *J. Organometal. Chem.*, **18**, 189 (1969).

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[9] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[10] J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *ibid.*, **9**, 2397 (1970).

[11] The program used for data reduction was Raymond's UCFACS, itself a modification of Doedens and Ibers' PIKOUT. Other computer programs used included Zalkin's FORDAP Fourier summation program, Hamilton's GONO general absorption program, Iber's NUCLS group least-squares refinement program based upon Busing and Levy's ORFLS, Busing and Levy's ORFFE, Johnson's ORTEP plotting program, and Corfield's RANGER weighting analysis programs. All computations were performed on a CDC 6400 computer.

[12] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[13] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[14] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[15] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

[16] D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE I

FINAL ATOMIC PARAMETERS

Atom[a]	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$
Pd	0.00000	0.07815 (7)	0.25000	1.52 (2)	7.8 (1)	15.2 (1)	0.0
Cl	0.09716 (7)	0.2994 (2)	0.25000	1.86 (4)	9.1 (2)	26.8 (4)	−0.45 (7)
C_1	0.1933 (3)	−0.2669 (8)	0.25000	1.6 (2)	13 (1)	30 (2)	0.5 (3)
N_1	0.1424 (2)	−0.1153 (6)	0.25000	1.5 (1)	8.2 (7)	26 (1)	0.0 (2)
C_2	0.0690 (3)	−0.1263 (7)	0.25000	1.8 (1)	9.6 (9)	15 (1)	0.6 (3)
N_2	0.0387 (2)	−0.2886 (5)	0.25000	1.5 (1)	9.1 (7)	20 (1)	0.2 (2)
H_1	0.0621	−0.4045	0.25000				
H_2	0.1581	−0.0017	0.25000				

[a] x, y, and z are fractional orthorhombic coordinates. Anisotropic thermal parameters are in the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$; here $\beta_{13} = \beta_{23} = 0$ because all atoms lie on the mirror plane at $z = 0.25$. The standard deviation of the least significant figure is given in parentheses.

anisotropic thermal motion assumed for all atoms resulted in $R_1 = 0.035$ and $R_2 = 0.049$. A difference electron density map calculated at this point clearly revealed an H atom bound to each of the crystallographically independent N atoms. These H atoms appeared as peaks of 0.9 and 0.6 e Å^{-3}. The map contained no peaks larger than 0.9 e Å^{-3}.

In space groups *Cmcm* and *C2cm* the methyl groups of the ligand are required to lie on a mirror plane. This condition limits the positions that the H atoms can occupy in a static model. Attempts to fit the residual density in the region of the methyl groups to either ordered or disordered static models were not successful. Therefore the methyl groups were assumed to be freely rotating and a fixed contribution from freely rotating methyl groups was included in subsequent structure factor calculations. It is also possible that the methyl H atoms are ordered and that the true space group is *Cmc*2$_1$. However, the resulting deviations from *Cmcm* would be so small that there would undoubtedly be singularity problems in attempting to refine the structure in the alternative space group.

Although refinement had converged, several intense low-order reflections had F_o significantly less than F_c, suggesting secondary extinction. An extinction parameter[17] was included as a variable and three additional cycles of full-matrix refinement with the H atoms included as fixed contribution to F_c gave final values for R_1 and R_2 of 0.030 and 0.038, respectively. The extinction correction markedly improved the agreement of the intense low-order planes. The standard deviation of an observation of unit weight was 1.27.

A final difference electron density map calculated from the 599 data used in the refinement showed no peak greater than 0.6 e Å^{-3}. A final structure factor calculation for all 737 data gave $R_1 = 0.063$ and $R_2 = 0.040$. All reflections with $F_o^2 < \sigma(F_o^2)$ had $F_c < 2\sigma(F_o)$.

The final structural parameters appear in Table I. A list of $10|F_o|$ and $10|F_c|$ is available.[18]

Description and Discussion

The numbering scheme and a perspective view of the molecule are shown in Figure 1. The sizes and shapes of the atoms are determined by the vibrational ellipsoids associated with the final anisotropic thermal parameters and by the perspective view. Interatomic distances and angles computed from the final atomic parameters of Table I appear in Table II and Figure 1.

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)

Pd–Cl	2.387 (1)	Cl–Pd–Cl	94.49 (7)
Pd–C_2	1.948 (5)	Cl–Pd–C_2	93.0 (2)
C_2–N_1	1.327 (7)	C_2–Pd–C_2'	79.5 (3)
N_1–C_1	1.441 (7)	Pd–C_2–N_2	115.5 (4)
C_2–N_2	1.309 (6)	Pd–C_2–N_1	126.3 (4)
N_2–N_2'	1.395 (8)	N_1–C_2–N_2	118.2 (4)
N_2–H_1	0.9	C_2–N_1–C_1	126.1 (4)
N_1–H_2	0.9	C_2–N_2–N_2'	114.8 (3)

The estimated standard deviations for the distances and angles were derived from the inverse least-squares matrix for the final refinement.

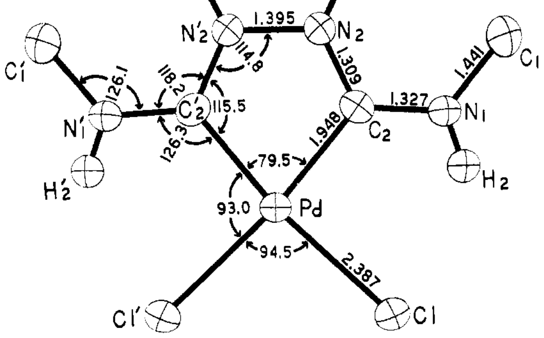

Figure 1.—Numbering scheme and view of the $[(CH_3)_2C_2N_4H_4]$-$PdCl_2$ molecule.

From Figure 1 it is readily apparent that the compound does not have structure **2** as originally proposed.[1] Rather a molecule of hydrazine has added to two cis isocyanide ligands to give a monomeric four-coordinate Pd(II) complex containing a novel –C–N–N–C– chelate skeleton which bonds to the Pd atom through carbon.[19,20] To our knowledge this represents the first definitive X-ray crystallographic evidence that coordinated isocyanides undergo chelative addition with nucleophiles. Chelate formation has been previously proposed[4] for the addition of borohydride ion to (C_5H_5)-$FeCO(CNCH_3)_2^+$. Simple addition of nucleophiles to coordinated isocyanides is now well documented,[3,5,8] and the structure of a complex arising from the addition of ethanol to a phenyl isocyanide complex of Pt(II) has been reported.[5]

In space group *Cmcm* the complex is required to be planar and possess *mm*-C_{2v} symmetry. The coordination geometry about the Pd atom is somewhat distorted from square planar, the major distortion being the C–Pd–C angle of 79.5 (3)° imposed by the chelate ring. The Pd–C distance[21] of 1.948 (5) Å is essentially identical with the Pt–C distance of 1.98 (2) Å found[5] for a monodentate isocyanide adduct. The Pd–Cl distance of 2.387 (1) Å is longer than the Pd–Cl distance of 2.31 Å

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[17] W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967).

[18] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C., 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[19] Rouschias and Shaw[20] independently proposed that **2** is monomeric and contains the –C–N–N–C– chelate skeleton. However, they did not deduce the correct arrangement of H atoms in the ligand.

[20] G. Rouschias and B. L. Shaw, *Chem. Commun.*, 183 (1970).

[21] The interatomic distances reported differ from those obtained earlier[2] by as much as 0.12 Å. However, in no case are the differences more than three times the estimated error for the earlier determination. In all future discussions the more precise results presented here should be used.

found in $PdCl_2$[22] but similar to the average Pt–Cl distance of 2.37 (1) Å found[5] for the ethanol adduct of a platinum (II) isocyanide complex.

The C–N and N–N bond distances of the chelate ring indicate some multiple-bond character for these bonds and are similar to the distances found in diformylhydrazine[23] and diacetylhydrazine.[24] The C–N distances are 1.325 (4) and 1.341 (8) Å in these compounds, whereas the C_2–N_2 distance here is 1.309 (6) Å; the N–N distance of 1.395 (8) Å found here is identical with 1.392 (7)[23] and 1.396 (9) Å[24] in the hydrazine derivatives. The N–N distance in hydrazine is 1.46 Å.[25]

The C_2–N_1 distance of 1.327 (7) Å is not significantly different from the C_2–N_2 distance and indicates multiple-bond character for the C–N bond external to the ring. This distance also implies that there will be a large barrier to rotation about the C_2–N_1 bond and that cis–trans isomerism about this bond might be observed under certain conditions. Indeed, in the closely related complex resulting from the addition of methylhydrazine to $Pt(CNCH_3)_4^{2+}$ both isomers occur in the same molecule.[26]

A projection of the structure along *c* is shown in Figure 2. The molecular plane of the complex is normal to the *c* axis of the crystal, and the molecules are stacked to form infinite chains parallel to *c*. The interplanar distance is *c*/2 (3.420 Å) and the Pd···Pd distance is 3.606 Å.

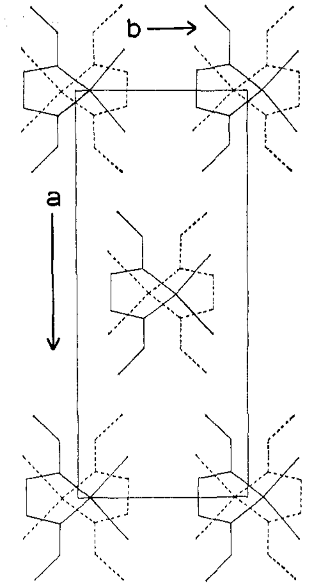

Figure 2.—The crystal structure of $[(CH_3)_2C_2N_4H_4]PdCl_2$ projected along the *c* axis.

Acknowledgments.—We thank Professor A. L. Balch for supplying the sample and for several helpful discussions. This research was supported by the National Science Foundation under Grant GP-12299 and a University of Arizona Institutional grant. We thank the University of Arizona Computer Center for an allocation of computer time.

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(26) W. M. Butler and J. H. Enemark, to be submitted for publication.

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Triglycine Autocatalysis of the Reaction between Copper–Triglycine and Ethylenediaminetetraacetate Ion

BY GARY R. DUKES, G. K. PAGENKOPF, AND DALE W. MARGERUM*

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The reaction between copper–triglycine ($CuH_{-2}L^-$) and EDTA is catalyzed by the released triglycinate ion (L^-). This autocatalysis reaction is shown to proceed *via* the bis-triglycine complex, $CuH_{-2}L_2^{2-}$, which is attacked more readily by $EDTA^{4-}$ than is the mono complex, $CuH_{-2}L^-$. Steric hindrance prevents EDTA from being an effective nucleophile with the mono complex and the postulated role of the second triglycine in the autocatalysis process is to facilitate the formation of a complex with only one Cu–N(peptide) bond. The bis complex is more readily converted to such a form than is the mono complex and this form does not sterically hinder nitrogen coordination by EDTA to a planar copper site. The detailed kinetic dependence of L^-, OH^-, and $EDTA^{4-}$ is accounted for including the appearance of rate maxima as a function of pH and L^- concentration and limiting rates at high EDTA concentrations.

Introduction

The transfer of copper ion from the copper(II)–triglycine complex to ethylenediaminetetraacetate ion is catalyzed by the released triglycine in solutions above pH 8. The exchange reaction is given in eq 1 where L^- is the glycylglycylglycinate ion and $CuH_{-2}L^-$ is the complex in which two protons are ionized from the peptide nitrogens. EDTA is a poor nucleophile in its reaction with $CuH_{-2}L^-$ and the manner in which a second triglycinate ion activates the transfer of copper to EDTA is of interest. Steric factors are important in controlling which ligands are able to react as nucleophiles with $CuH_{-2}L^-$, and EDTA, as well as other ligands with only tertiary nitrogens, is sterically hin-

$$\mathrm{CuH_{-2}L^-} + \left[\begin{array}{c}\mathrm{EDTA^{4-} + 2H_2O} \\ \uparrow\downarrow \\ \mathrm{HEDTA^{3-} + H_2O}\end{array}\right] \longrightarrow \left[\begin{array}{c}\mathrm{2OH^-} \\ \\ \mathrm{OH^-}\end{array}\right] + \mathrm{CuEDTA^{2-} + L^-} \qquad (1)$$