The Isomers of α-Amino-acids with Copper(II). Part 5.[1,†] The *cis* and *trans* Isomers of Bis(glycinato)copper(II), and their Novel Thermal Isomerization

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The crystalline *trans* isomer of bis(glycinato)copper(II) is, contrary to many reports, a monohydrate. The dehydration of the solid *cis*-monohydrate at sufficiently high temperatures leads to the anhydrous *trans* complex, which readily rehydrates to give the *trans*-monohydrate, a useful preparative technique. Kinetic and thermochemical studies have been made on the loss of water from the *cis* isomer and possible mechanisms for the reaction are discussed.

THE bis(amino-acidato)-complexes of copper(II) have been studied for many years because of their utility and inherent interest. It transpires that, although polymorphism of one kind or another is widespread,[2,3] the one firmly established case of geometric isomerism is still that of bis(L-alaninato)copper(II) where crystallography has shown the nature of the co-ordination of the copper atom in both *cis*[4] and *trans* isomers.[5] The first geometric isomers discovered for a copper(II) amino-acid complex were the modifications of bis(glycinato)copper(II), [Cu(glyO)$_2$], but in that case only one crystal structure is as yet available,‡ that of *cis*-bis(glycinato)copper(II) monohydrate.[6] Our analyses for the *trans* modification of [Cu(glyO)$_2$] did not agree with the frequently cited composition as a dihydrate;[3,7-11] we find it to be a monohydrate.

Acicular [Cu(glyO)$_2$]·H$_2$O was discovered by Boussingault[12] in 1841; Mauthner and Suida[13] in 1890 described the preparation of a lustrous platy modification of [Cu(glyO)$_2$], also a monohydrate. In 1912, Ley and Wiegner[14] suggested, by analogy with the complexes of platinum, that the two modifications might be *cis* and *trans* isomers. The lustrous platy modification was again described as a new compound by Engeland[15] in 1938. Grinberg and Gol'braith[16] published a scholarly but largely overlooked report in 1941; again the platy modification was described as a monohydrate. Further, they measured the aqueous solubility of the *cis*-monohydrate at 0 °C as 0.521 g in 100 cm^3 and of the *trans*-monohydrate as 0.302 g in 100 cm^3, the solubility of the metastable *cis* solution decreasing to that of the *trans*. In 1961, Tomita[7] again described the preparation and characterization of both isomers, making no reference to earlier work. He described the platy *trans* modification as a dihydrate. This is the only report cited in a large number of later i.r. studies.[3,7-11] However, in a neglected report, Ablov *et al.*[17] again showed the *trans* isomer to be a monohydrate. Describing the diffuse-reflectance spectra, Yasui and Shimura[18] reported the *trans* modification as a monohydrate, and in the only e.s.r. study of

these *cis–trans* isomers[19] the *trans* isomer was also cited as a monohydrate. However, when last described in 1976, in a detailed i.r. study, the complex was yet again described as a dihydrate.

In view of the limited and contradictory analytical data published and the fact that these complexes have occupied a central position in the study of *cis–trans* isomers by i.r. spectroscopy[20] and other means, we have undertaken a detailed study of these complexes by a variety of analytical techniques. Further, although both Ablov and Tomita noted that the product of dehydrating both isomers was the same, the fact that this represents a most unusual solid-state reaction was not appreciated. We have hence investigated this novel thermal isomerization by a variety of techniques, identified and characterized four modifications of bis(glycinato)copper(II) (*i.e.* anhydrous *cis*-, anhydrous *trans*-, *cis*-monohydrate, and *trans*-monohydrate), and studied their interconvertibility.

RESULTS

State of Hydration of the Complexes.—Samples of the *cis* and *trans* isomers prepared by conventional methods and dried in air were subjected to thermogravimetric analysis (t.g.a.). As previously noted,[17] very distinctive patterns are observed, the *trans* isomer losing its single water molecule of crystallization (7.8%) much more easily (at 100—127 °C) than the *cis* isomer (7.8% at 145—181 °C). No evidence for a dihydrated *trans* isomer was found even from freshly prepared samples, and a sample of the *trans*-monohydrate stored in a humidifier for 10 d showed no weight increase, t.g.a. again revealing 7.8% water loss (at 100—127 °C). Although losing its water readily on heating, the *trans* isomer may be stored indefinitely over fairly strong desiccants (*e.g.* CaCl$_2$) with no loss of water.

The electronic spectra of the two modifications in the visible regions were measured by diffuse reflectance and as aqueous solutions (Table 1). A further check on the state

TABLE 1

Electronic spectra [a] of samples of bis(glycinato)copper(II)

	λ/nm		ε/
	solid	solution	dm^3 mol^{-1} cm^{-1}
cis-monohydrate	630	630	48.1
trans-monohydrate [a]	600	630	47.9
anhydrous *trans* [b]	600		
anhydrous *cis* [b]	630		

[a] Identical values were obtained for a sample made by thermal isomerization. [b] Freshly prepared and simultaneously analyzed by i.r. spectroscopy and t.g.a.

of hydration of the isomers was made by measuring the molar absorption coefficients of their aqueous solutions; these are (within experimental error) identical, both being calculated for a monohydrate. The spectrum in solution is similar to that of the *cis* isomer (whether hydrated or not) recorded by diffuse reflectance. Correlations between the solid state and solution are fraught with pitfalls and no firm conclusion should be drawn from this observation; Laurie [2] has discussed in detail some problems in such comparisons. We further measured the spectra of a saturated solution of the *trans* and of the metastable ' supersaturated ' *cis* isomer: these are identical with the spectra recorded for dilute solutions prepared from the *cis* or *trans* isomer. This is not too surprising. In an earlier study [2a] of the isomeric L-alaninato-complexes such solutions had very similar electronic spectra, although their asymmetry factors were different.

The *trans*-monohydrate has also been analyzed by X-ray powder photography (Debye–Scherrer method). Our results are identical with those reported by Tomita for his ' dihydrate ' and by Ablov for a monohydrate.* The ' dihydrate ' has frequently been reported as the complex used for i.r. studies. In Table 2 we give our results with

TABLE 2

Infrared spectra (cm^{-1}) [a] of *trans*-[Cu(glyO)$_2$]·H$_2$O Monohydrate

authentic [b] monohydrate	isomerized [c]	Nakamoto [d] ' dihydrate '	Assignment [d]
1 595vs,vbr	1 590vs,vbr	1 593vs	$\nu_{asym}(CO_2)$
1 430w	1 430w	1 435w	$\delta(CH_2)$
1 385s	1 387s	1 392s	$\nu_{sym}(CO_2)$
1 328m	1 326s	1 331m	$\delta_w(CH_2)$
1 190vw (sh)	1 190vw (sh)	1 199w (sh)	$\delta_t(CH_2)$
1 155s	1 153s	1 151s	$\delta_t(CH_2)$
1 060m	1 060m	1 058s	$\nu(C-N)$
948m	945w	942w	$\nu(C-N)$
916ms	911ms	909ms	$\nu(C-C)$
740m	740m	737m	$\delta(CO_2)$

[a] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad, ν_{asym} = antisymmetric stretching, ν_{sym} = symmetric stretching, δ = bending, δ_t = twisting, and δ_w = wagging. [b] Prepared by solution method (a) of Experimental section. [c] Prepared by thermal method (a) of Experimental section. [d] Ref. 11.

TABLE 3

Analytical results for *trans*-[Cu(glyO)$_2$]·H$_2$O

	Analysis (%)				Temperature of [a] water loss
	C	H	N	H$_2$O	
Calc.	20.9	4.40	12.2	7.85	
Authentic preparation [b]	20.75	4.35	11.65	7.80	100—127
Thermal isomerization method [c]	20.8	4.30	11.5	7.70	100—127

[a] t.g.a. at 10 °C min^{-1} with 10 l min^{-1} N$_2$. [b] Method (a) of Experimental section on *trans*-monohydrate. [c] Method (a) of Experimental section.

some typical i.r. results [11]; these spectra are clearly those of the same complex. The significance of the hydration number of these complexes should not be underestimated; e.g. i.r. differences have been attributed [3] to their different state of hydration. In Table 3 we report some typical analytical results for *trans*-bis(glycinato)-

* The results of the X-ray studies of all four modifications are tabulated in Supplementary Publication No. SUP 22498 (7 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

copper(II) monohydrate. These results have been exhaustively checked.

Thermal Isomerization.—Ablov *et al.*[17] produced two dehydrated forms of [Cu(glyO)$_2$] and noted their interconvertibility. They did not however fully characterize this change nor appreciate its significance and as has been noted their work has been largely overlooked. Their results led us to believe that besides its intrinsic interest this novel solid-state reaction might provide an easy method of preparing the *trans*- from the *cis*-monohydrate. The difficulty of carrying out this conversion on a small scale has been noted.[3,11] Our method may be of use for isotopically labelled samples.

Tomita [7] also noted that only one complex was produced on dehydrating the two isomers: however, he believed that the *trans* isomer was being isomerized. Our results establish that it is in fact the *cis* isomer which undergoes a thermal rearrangement.

cis-Bis(glycinato)copper(II) monohydrate may be dehydrated to give both an anhydrous *cis* complex (Ablov's β-isomer) and an anhydrous *trans* isomer (Ablov's α-isomer). Details of the methods used for dehydration are given in the Experimental section. Briefly, if the complex is dehydrated under mild conditions (<140 °C) the anhydrous *cis* isomer is obtained, whereas under more vigorous conditions (>180 °C) the anhydrous *trans* isomer is obtained. These complexes may be hydrated by storage in water vapour for 48 h.

The complexes have all been identified by i.r., X-ray powder photographs, visible diffuse reflectance, and thermogravimetric analysis. The i.r. spectra are particularly useful in such identification, and in Table 2 such spectra are compared for conventionally prepared and thermally isomerized samples of the *trans* isomer. The X-ray powder photograph of the *trans* isomer prepared in this way is identical with that of a conventionally prepared sample.

The i.r. spectra of the four complexes in the ' fingerprint ' region were sufficiently different to be characteristic (Figure 1). The four complexes which we assign as *cis*-monohydrate, *cis*-anhydrous (Ablov's β-isomer), *trans*-monohydrate, and *trans*-anhydrous (Ablov's α-isomer) show as expected in the i.r. a clear relationship between geometrically corresponding hydrated and anhydrous forms.

With samples of the anhydrous *cis* isomer dispersed in potassium bromide discs it was possible to show the conversion into the anhydrous *trans* isomer. This change was easier if the sample was already dispersed in a disc, being complete in *ca.* 5 min at 150 °C: by contrast, complete conversion of an isolated sample required 5—10 min at 200 °C. The mechanical fracture of crystals while making the disc, pressure, or even bromide catalysis are possible explanations of this observation.

Thermochemical Studies.—By differential scanning calorimetry (d.s.c.) we have measured the enthalpy of dehydration of the *cis* and *trans* isomers. The temperatures associated with the transitions are very similar to those recorded by t.g.a., the *trans* isomer losing its water more easily (110—145 °C) than the *cis* (160—195 °C). However, if the sample pan of the calorimeter were tightly packed for the *cis* isomer *alone* (in common with the results of Ablov *et al.*[17]) we recorded a definite endothermic effect and water was lost more rapidly (168—178 °C); the enthalpy change associated with this process was the same as that for the conversion in less tightly packed samples. The results of the calorimetric studies are recorded in Table 4 with an

TABLE 4

Enthalpy of dehydration of cis- and trans-[Cu(glyO)$_2$]·H$_2$O

Complex	ΔH/kJ mol^{-1}	No. of determinations	Calibrant
cis	33.8 ± 2.4	4	In
	31.5 ± 2.2	4	Benzil
	30.9 ± 2.0	5	In
	32.1 ± 1.9	overall	
trans	41.2 ± 1.8	4	In

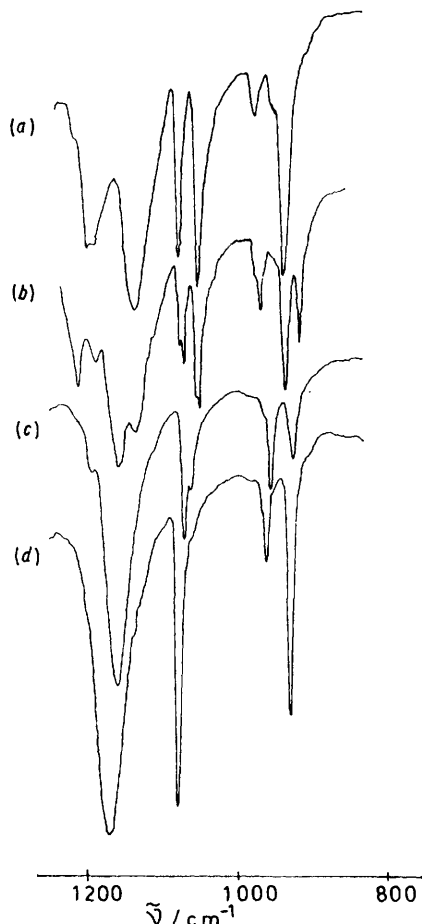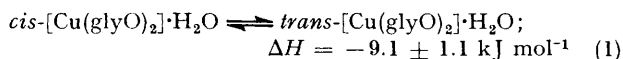indication of the number of individual determinations and calibrant used.

FIGURE 1 Infrared spectra in the region 800—1 200 cm^{-1} of the isomers: (a) cis-hydrate; (b) cis-anhydrous; (c) trans-anhydrous; (d) trans-hydrate

From the calorimetric results, we may (since the product of the dehydration of the cis and trans isomers is the same) calculate the enthalpy difference * between cis- and trans-monohydrate [equation (1)]. In common with Ablov et al.[17] we find that the trans isomer is the more thermodynamically

$$cis\text{-}[Cu(glyO)_2]\cdot H_2O \rightleftharpoons trans\text{-}[Cu(glyO)_2]\cdot H_2O;$$
$$\Delta H = -9.1 \pm 1.1 \text{ kJ mol}^{-1} \quad (1)$$

stable. However, our value of 9.1 kJ mol^{-1} for ΔH is somewhat higher than their 1.8 kJ mol^{-1}. The enthalpy of dehydration of bis(glycinato)copper(II) has also been reported by Bernard et al.[21] as 56 kJ mol^{-1}. In that work it

* This value is not an absolute thermodynamic quantity, since we have made no attempt to incorporate specific-heat corrections.

is not clear which isomer of the complex was studied. Further, in related papers,[22] when potentially optically active amino-acids were studied, it is not clear whether racemic or optically active ligands have been used. In the case of alanine it must be presumed that the racemic ligand was used since both cis- and trans-bis(L-alaninato)copper(II) are well studied [4,5] anhydrous complexes.

The latent heat of vaporization of water is [23] 40.6 kJ mol^{-1} at 100 °C and 36.9 kJ mol^{-1} at 170 °C. This is close to the enthalpy of dehydration of the trans but not cis isomer, presumably because of the concurrent exothermic isomerization.

Attempts to study the isomerization of the anhydrous cis complex (we know this to occur from our i.r. work) were, however, unsuccessful: no reaction could be detected in the calorimeter before the onset of decomposition at 250 °C.

Direct Observations and Kinetic Results.—Using relatively large (ca. 3—4 mm long) crystals of the cis isomer, the isomerization could readily be followed on the stage of a Koffler block. The crystals are blue and translucent. However, on heating to between 160 and 170 °C dark nuclei developed within the crystals, often close to a recognizable defect. On reaching a critical size the nuclei spread rapidly along the long axis of the crystal and drops of water vapour condensed on the cover slip.

Isothermal kinetic studies of the dehydration have been carried out. The rate of loss of water from the complex is to a good approximation first order, fitting equation (2) well,

$$\log [a/(a - x)] = kt \quad (2)$$

where a = initial mass of complex and x = mass of anhydrous complex. This equation has been shown to hold [24] for various solid-state reactions. However, equation (2) has nearly the same overall form as that [(3)] derived [25,26] for a random nucleus rapidly expanding in two dimensions, the only difference being that a finite intercept is predicted by (3). Here α = fraction of dehydration and k = rate of

$$\log (1 - \alpha) = c - kt \quad (3)$$

nucleation. Intercepts were frequently encountered in our experiments: however, it is possible that these were due in the main to the time required for thermal equilibration within the furnace and their physical significance is not clear.

For solid-state reactions it is generally found [25] that the activation energy is relatively independent of crystal size, although individual rate constants may vary considerably. This is in line with our findings, and in Table 5 we sum-

TABLE 5

Kinetic results [a] for reactions of solid [Cu(glyO)$_2$]·H$_2$O

Experiment	E_a/ kJ mol^{-1}	$\log_{10}A$	Temperature range $(\theta_c/°C)$	Crystal size [b]
1	97.6 ± 4	9.28	108—132	medium
1a	193 ± 14	20.9	166—182	medium
2	109 ± 10	10.7	114—130	small to medium
2a	164 ± 5	17.8	150—170	small to medium
3	163 ± 10	17.4	156—176	medium

[a] Abstracted from detailed Tables in the Ph.D. thesis of P. O' Brien, University of Wales, 1978. [b] Results of four independent preparations with recrystallization from ethanol–water: medium, length not greater than 3 mm; small to medium, length not greater than 2 mm.

marize kinetic results for a number of samples {including one sample, number 3, prepared some years earlier; this sample showed similar behaviour in all experiments to that of our freshly prepared cis-[Cu(glyO)$_2$]·H$_2$O}.
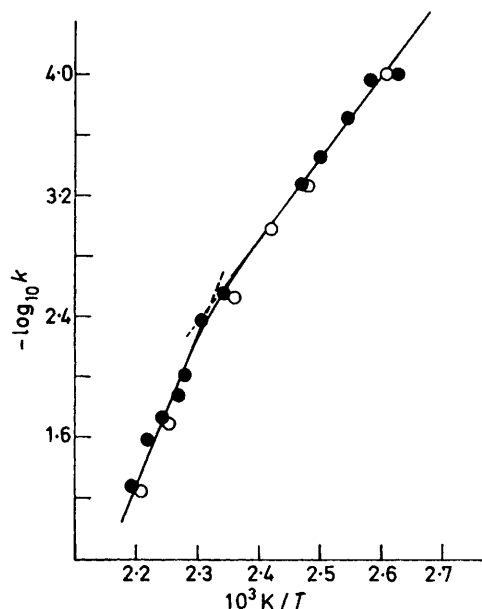

FIGURE 2 Temperature dependence of the rate of dehydration of cis-bis(glycinato)copper(II) monohydrate: (●) experimental points, (○) simulated points

The kinetic results clearly define two processes; dehydration alone with an activation energy close to 100 kJ mol^{-1} and another process with a much higher activation energy of ca. 170 kJ mol^{-1} (dehydration–isomerization). The variation of activation energy between individual determinations is perhaps higher than might be expected from the literature. However, data for such reactions are rare, and duplicate determinations rarer. In Figure 2 we show an Arrhenius-type plot for the dehydration of a single preparation of cis-bis(glycinato)copper(II) over a wide temperature range (108—182 °C). It is most striking that two linear regions are observed, for $T <$ ca. 140 °C and for $T >$ ca. 160 °C and that the rate profile is curved between these points. The activation energy and pre-exponential factors have been determined for each process by a least-squares analysis within these linear regions. The validity of the analysis has been checked by plotting values of $k_{obs.}$ calculated from equation (4); these are superimposed on Figure 2. Here k_d = rate constant for dehydration and

$$k_{obs.} = k_d + k_g \qquad (4)$$

k_g = rate constant for simultaneous dehydration–isomerization.

We confirmed by i.r. spectroscopy that the reaction product was indeed the anhydrous cis isomer in the low-temperature region, a mixture of cis and $trans$ isomers at intermediate temperatures, and the anhydrous $trans$ isomer at high temperature. Thus, the magnetic results and discussion relating to a sample of ' anhydrous bis(glycinato)copper(II) ' described as cis (sic) (K. E. Hyde, P. L. Bocko, M. Lynch, R. Adams, and G. Kokoszka, $Inorg.$ $Chim.$ $Acta$, 1976, **19**, 51) and made by ' heating the hydrate at 175 °C for several hours ' will need revision, since

that sample is almost certainly the anhydrous $trans$ isomer. There is a grave misconception in that paper, that ' thermal dehydration of hydrates where the water is bound to the copper atom by long bonds (greater than 2.05 Å) results in little structural rearrangement. . . . For [Cu(glyO)$_2$]·H$_2$O dehydration of the . . . long-bond hydrate results in a normal anhydrous complex with retention of the five-membered chelate ring.' This, the last remark in that paper, is, of course, wrong.

DISCUSSION

Studies of the solid-state reactions of co-ordination compounds are relatively rare [25] and indeed we believe this to be the first example of solid-state cis–$trans$ isomerization for a square-planar system. In the Scheme we summarize the processes we have observed. The dehydration and isomerization both have two possible paths, dependent on temperature. On the basis of our results, it is possible to predict with fair accuracy the product of dehydration at a given temperature.

Isomerizations of square-planar complexes are known to occur by both inter- and intra-molecular processes; $e.g.$ in the analogous platinum complexes it has been shown that photochemically the isomerization happens in an intramolecular manner, whereas in solution an intermolecular mechanism occurs.[27,28] Indeed, the normal method of isomerizing cis-bis(glycinato)copper(II) in solution depends on an intermolecular process, as indicated both by the catalysis by glycine of the isomerization [19] and the exchange kinetics of the system.[29]

Activation energies for solid-state reactions are scarce, but our values are in line with those reported. A value of ca. 100 kJ mol^{-1} is typical for an activation energy associated with dehydration alone. Our higher activation energy of ca. 170 kJ mol^{-1} is in line with some recorded for isomerization.[24] Such activation energies have been interpreted in terms of an intramolecular mechanism, viz. chelate-ring opening or a twist. The other major possibility is that the concerted reaction proceeds by an ' aquation ' mechanism in which one glycine is transiently displaced from the square plane by a leaving water molecule. Distinction between these possibilities is difficult, and, as is so often the case in copper(II) systems, kinetic lability excludes many otherwise sensible experiments.
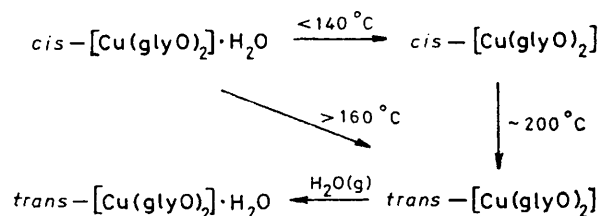
SCHEME Transformations observed

$Other$ $Complexes.$—We have prepared the bis(DL-phenylalaninato)- and the bis(L-alaninato)-copper(II) complexes in both their cis and $trans$ modifications. No evidence of isomerization could be detected on heat-

ing at 200 °C for times up to *ca.* 25 min (when considerable charring had occurred).

EXPERIMENTAL

Reagents.—B.D.H. AnalaR reagents were used throughout with the exception of amino-acids which were B.D.H. chromatographically homogeneous grade.

Preparation of Complexes.—cis-*Bis(glycinato)copper*(II) *monohydrate.* Hot solutions containing stoicheiometric amounts of copper(II) sulphate and glycine were neutralized with concentrated sodium hydroxide and ethanol was added to the point of precipitation. On cooling, the product separated as fine needles, which were recrystallized once from ethanol–water (1 : 1).

trans-*Bis(glycinato)copper*(II) *monohydrate.* (*a*) A suspension of the *cis* isomer (*ca.* 10% w/v) was heated on a water-bath. After 5—6 h the *trans* modification had separated as lustrous platelets, which were removed from the hot solution and dried in air. Alternatively, the reaction was allowed to proceed overnight (up to 16 h), producing an identical product.

(*b*) A suspension of the *cis* isomer (*ca.* 10% w/v) was stirred or shaken at room temperature for 4—5 d, when small platelets of the *trans* isomer separated and were collected.

Methods of Thermal Isomerization.—(*a*) Samples of the *cis*-monohydrate (5—10 mg) were heated in the thermogravimetric balance (10° min⁻¹) until all water had been removed (*ca.* 205 °C). This produced the anhydrous *trans* isomer, and storing this complex in a humidifier for 48 h gave total conversion into the *trans*-monohydrate.

(*b*) Samples of the *cis*-monohydrate were heated isothermally in an oven or on the thermogravimetric balance at temperatures >180 °C for 15—20 min. This produced the anhydrous *trans* isomer which could be treated as above.

(*c*) Dehydrating the *cis*-monohydrate carefully during several hours at temperatures <140 °C to constant weight produced the anhydrous *cis* isomer.

(*d*) The anhydrous *cis* isomer was heated at >180 °C for 5—10 min, producing the anhydrous *trans* isomer.

Methods (*b*) and (*d*) have a much higher chance of charring the sample than does (*a*). If large (>30 mg) samples are dehydrated, substantially longer than 2 d may be required for the complete uptake of water by the anhydrous product to give the *trans*-monohydrate. All four modifications of [Cu(glyO)₂] prepared by all methods have been fully characterized by microanalysis, i.r. spectroscopy, and X-ray powder photographs, and typical analyses are reported (Table 3). Hydrated complexes have been further analyzed by thermal methods (d.s.c. and t.g.a.).

Bis(L-*alaninato*)*copper*(II) *and Bis*(DL-*phenylalaninato*)-*copper*(II).—These complexes in their *cis* and *trans* modifications were prepared by known methods [2,4] and characterized by microanalysis and i.r. spectroscopy.

Methods.—Infrared spectra were recorded for Nujol or hexachlorobutadiene mulls (600—3 500 cm⁻¹) using a Perkin-Elmer 457 spectrometer. A number of spectra were obtained in potassium bromide discs and gave identical results. X-Ray powder photographs were obtained by the Debye–Scherrer method using Cu-K_α radiation (λ 1.541 8 Å). A Perkin-Elmer D.S.C.IB apparatus was used for differential-scanning calorimetry. It was calibrated frequently using indium metal. Independent calibration with the melting-point standard benzil gave a further check, consistent results being obtained. Reported heats are for

samples weighing between 4 and 10 mg at a heating rate of 8° min⁻¹ under a nitrogen flow of *ca.* 10 l min⁻¹. Thermogravimetric analysis was performed using a Stanton Redcroft TG-750 Thermobalance. Routine analysis was carried out under nitrogen (10 l min⁻¹), the sample size lying between 6 and 10 mg.

In our experiment on isothermal weight loss, described in the text, the sample was plunged into the furnace preheated to the required temperature, to minimize errors due to equilibration. Temperature was recorded with a thermocouple Pt:Pt,Rh (13%), with ice–water as reference.

X-Ray Powder Photography.—All photographs were recorded by the Debye–Scherrer method. The data of Tomita [7] gave no indication of line intensity, making comparison somewhat difficult. The data published by Ablov *et al.* [17] were in the form of small diagrams of normalized intensity; only the main lines (relative intensity >50%) have been measured for inclusion in SUP 22498 (accuracy of measurement ∓0° 20′).

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