The Co-ordination Chemistry of Divalent Cobalt, Nickel, and Copper. Part 13.† Characterization and Stability Constants of Copper(II) Species isolated from Mixed-ligand Solutions; Crystal Structure of the Complex (Pyridine-2,6-dicarboxylato)(*N,N,N′,N′*-tetramethyl-1,3-diaminopropane)copper(II)‡

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Six-co-ordinate complexes [Cu(pydca)(L)(H_2O)]·H_2O and five-co-ordinate complexes [Cu(pydca)(L)], where pydca = pyridine-2,6-dicarboxylate, L = en (1,2-diaminoethane), tmen (*N,N,N′,N′*-tetramethyl-1,2-diaminoethane), pn (1,3-diaminopropane), or pen [1,2-di(pyrrolidin-1-yl)ethane], were isolated and characterized by thermogravimetric, calorimetric, spectrophotometric, magnetic, and stability constant measurements. A structure determination on [Cu(pydca)(tmpn)] (tmpn = *N,N,N′,N′*-tetramethyl-1,3-diaminopropane), which was monoclinic, with space group $P2_1/c$, $a = 14.970(2)$, $b = 7.290(1)$, $c = 14.822(2)$ Å, $\beta = 106.64(2)°$, $Z = 4$, indicated a distorted square-pyramidal co-ordination sphere with considerable steric interaction between the tertiary amine groups and the two carboxylate groups. The splitting of the ν_{sym}(COO) and ν_{asym}(COO) i.r. bands of all the above complexes having tertiary amine ligands was ascribed to the distortions resulting from this steric interaction. Stability constants for some complexes are reported.

For the past two decades the nature of low symmetry five-co-ordinate complexes, and the factors which lead to their stabilization, have been investigated in these laboratories. Different *modus operandi* were systematically attempted in order to isolate these complexes.[1–3] All attempts involved the use of mixed ligands. In this project the complexes isolated from solutions containing equimolar amounts of pyridine-2,6-dicarboxylate (pydca) and copper(II), and varying amounts of 1,2-diaminoethane (en), 1,3-diaminopropane (pn), *N,N,N′,N′*-tetramethyl-1,2-diaminoethane (tmen), *N,N,N′,N′*-tetramethyl-1,3-diaminopropane (tmpn), or 1,2-di(pyrrolidin-1-yl)ethane (pen) were studied. These diamine ligands were selected so that the effect of variation in steric hindrance on the Cu(pydca) moiety could be investigated. This study was further motivated by the anomalous bands found in the i.r. spectra of Ni(pydca)(tmen)·2H_2O.[4] The two carboxylate groups of pydca in the compound were co-ordinated in almost identical fashion, but the ν_{asym}(COO) and ν_{sym}(COO) bands were split. It was hoped that the isolation, characterization, and *X*-ray structure determination of an analogous compound could elucidate the cause of this peculiar splitting.

Experimental

Preparations.—The ligand 1,2-di(pyrrolidin-1-yl)ethane was prepared as described in the literature.[5] All other ligands were purchased, but purified by distillation or recrystallisation prior to use. The starting material Cu(pydca)·2H_2O was prepared in an analogous manner to the method used in the preparation of Ni(pydca)·3.5H_2O.[3]

An accurately measured amount of Cu(pydca)·2H_2O (15.0 mmol) was dissolved in hot aqueous en solution (20 cm^3, 15.1 mmol). Hot 95% ethanol (100 cm^3) was added and the mixture was slowly cooled to 4 °C yielding blue crystals of Cu(pydca)(en)·2H_2O. Blue crystalline Cu(pydca)(pn)·2H_2O was similarly prepared.

Cu(pydca)·2H_2O (20 mmol) was dissolved in a boiling solution of tmen (25 mmol) in water (10 cm^3) and methanol (65 cm^3). After addition of boiling ethyl acetate (150 cm^3), the solution was slowly cooled to room temperature producing large blue crystals of Cu(pydca)(tmen)·2H_2O.

A mixture of ethyl acetate (20 cm^3) and diethyl ether (150 cm^3) was added to a hot solution of Cu(pydca)·2H_2O (10 mmol) and tmpn (11 mmol) dissolved in ethanol (40 cm^3).

Table 1. Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, for the non-hydrogen atoms of [Cu(pydca)(tmpn)]

Atom	x	y	z
Cu	2 348(0)	−345(0)	1 310(0)
N(1)	3 252(1)	748(2)	786(1)
C(2)	3 017(1)	1 079(3)	−139(1)
C(3)	3 647(2)	1 879(3)	−543(2)
C(4)	4 518(2)	2 370(4)	52(2)
C(5)	4 736(2)	2 074(3)	1 019(2)
C(6)	4 071(1)	1 248(3)	1 368(2)
C(7)	4 116(2)	892(3)	2 389(2)
O(1)	3 371(1)	152(2)	2 503(1)
O(3)	4 808(1)	1 356(3)	3 020(1)
C(8)	2 009(2)	558(3)	−621(2)
O(2)	1 558(1)	1(2)	−50(1)
O(4)	1 699(1)	709(2)	−1 479(1)
N(2)	2 454(1)	−3 392(3)	1 098(1)
C(21)	2 985(2)	−3 669(4)	410(2)
C(22)	2 936(2)	−4 416(5)	1 965(2)
N(3)	1 253(1)	−484(3)	1 838(1)
C(31)	1 518(2)	−897(4)	2 863(2)
C(32)	829(2)	1 395(4)	1 702(2)
C(9)	1 498(2)	−4 117(4)	682(2)
C(10)	839(2)	−3 765(4)	1 279(2)
C(11)	520(2)	−1 790(4)	1 294(2)

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† Part 12, J. G. H. du Preez, B. J. A. M. van Brecht, and I. Warden, *Inorg. Chim. Acta*, 1987, **131**, 259.

‡ *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue, pp. xvii—xx.

Table 2. Analytical data for compounds prepared as described in the Experimental section

	Analysis (%)*				Magnetic moment,
Complex	Cu	C	H	N	$\mu_{eff.}$
Cu(pydca)(en)·2H_2O	19.6 (19.6)	33.3 (33.3)	4.7 (4.7)	12.9 (12.4)	1.92
Cu(pydca)(en)	22.1 (22.0)	37.0 (37.4)	4.0 (3.8)	14.3 (14.5)	1.94
Cu(pydca)(pn)·2H_2O	18.6 (18.8)	35.6 (35.5)	4.9 (5.1)	12.4 (12.4)	1.91
Cu(pydca)(pn)	20.8 (21.0)	39.7 (39.7)	4.3 (4.3)	13.8 (13.9)	1.88
Cu(pydca)(tmen)·2H_2O	16.6 (16.7)	40.9 (41.0)	6.0 (6.1)	10.9 (11.0)	1.89
Cu(pydca)(tmen)	18.4 (18.4)	45.0 (45.3)	5.8 (5.6)	12.0 (12.2)	1.90
Cu(pydca)(tmpn)	17.7 (17.7)	46.9 (46.9)	5.9 (5.9)	11.6 (11.7)	1.92
Cu(pydca)(pen)·2H_2O	14.7 (14.7)	47.0 (47.2)	6.2 (6.3)	9.7 (9.7)	1.94
Cu(pydca)(pen)	16.0 (16.0)	51.6 (51.4)	5.8 (5.8)	11.0 (10.6)	1.91

* Calculated values are given in parentheses.

Table 3. Pertinent bands in the electronic and i.r. spectra[a]

	I.r. spectra (cm^{-1})						
	Carboxylate co-ordination		Pyridine co-ordination		Amine co-ordination	Electronic spectra (nm)	
	ν_{asym}(COO)	ν_{sym}(COO)			ν(Cu–N)	Solid reflectance	Solution[b]
Cu(pydca)(en)·2H_2O	1 630	1 380	683	442, 425	470, 480	780, 1 300 (br)	710 (28), 1 300 (32)[c]
Cu(pydca)(en)	1 630	1 380	685	430, 445	525	335, 550, 780, 1 250	
Cu(pydca)(pn)·2H_2O	1 635	1 370	683, 670	440, 430	495	560, 780, 1 310	650 (36), 1 050 (22)[c]
Cu(pydca)(pn)	1 630	1 380	695, 685	420—440	490	335, 560, 760, 1 300	
Cu(pydca)(tmen)·2H_2O	1 670, 1 625	1 380, 1 365	693, 672	450	475	730, 1 100 (br)	720 (70), 1 090 (36)[d]
Cu(pydca)(tmen)	1 672, 1 625	1 380, 1 365	693, 672	450	470	730, 1 100 (br)	
Cu(pydca)(tmpn)	1 655, 1 675	1 335, 1 350	690, 680 (sh)	435, 420		730, 1 000 (br)	730 (144), 1 000 (51)[d]
Cu(pydca)(pen)·2H_2O	1 631, 1 650, 1 675 (sh)	1 335, 1 360	688	425		720, 1 100 (br)	720 (104), 950 (52)[d]
Cu(pydca)(pen)	1 650, 1 670	1 335, 1 352	688	435		720, 950	
H_2pydca	1 700s	1 360	645m	420m			

[a] s = Strong, m = medium, sh = shoulder, br = broad. [b] ε/dm^3 mol^{-1} cm^{-1} given in parentheses. [c] 55% Ethanol. [d] 95% Ethanol.

Crystals of Cu(pydca)(tmpn) were formed slowly after cooling the mixture to room temperature.

Finely ground Cu(pydca)·2H_2O (20 mmol) was dissolved in a hot solution of pen (22 mmol) in ethanol (50 cm^3) and water (10 cm^3). After all the solid had dissolved, hot ethyl acetate (330 cm^3) was added. The resultant mixture was cooled to −15 °C and then kept at this temperature for 2 d. Large turquoise crystals of Cu(pydca)(pen)·2H_2O were obtained. Heating powdered Cu(pydca)(pen)·2H_2O to 100 °C resulted in formation of Cu(pydca)(pen).

The anhydrous complexes Cu(pydca)(en), Cu(pydca)(pn), and Cu(pydca)(tmen) were prepared by heating the corresponding hydrated complex to 150 °C.

Crystal-structure Determination of [Cu(pydca)(tmpn)].—*Crystal data.* $C_{14}H_{21}CuN_3O_4$, $M = 358.9$, monoclinic, space group $P2_1/c$, $a = 14.970(2)$, $b = 7.290(1)$, $c = 14.822(2)$ Å, $\beta = 106.64(2)°$, $U = 1\,549.9$ Å^3, $D_m = 1.51$, $D_c = 1.53$ g cm^{-3}, $Z = 4$, $\lambda = 0.710\,73$ Å, $F(000) = 748$, μ(Mo-K_α) = 13.6 cm^{-1}.

The space group and preliminary cell dimensions were obtained from Weissenberg photographs (Cu-K_α radiation). The dimensions were refined by least-squares methods using the angular settings obtained from 25 high-order reflections (Mo-K_α, graphite monochromated) measured on a Phillips PW1100 four-circle diffractometer. Intensity data were collected by the ω—2θ scan technique ($3 > \theta > 25°$). Of the 2 958 reflections measured, all 2 555 unique reflections [$I > 2\sigma(I)$] were used in the final refinement. Lorentz-polarization and absorption corrections[6] were applied.

The trial structure was obtained by Patterson and conventional Fourier techniques. All hydrogen atoms were located. Refinement was done using full-matrix least-squares methods, non-hydrogen atoms being refined anisotropically while the hydrogen atoms were refined isotropically and without positional restrictions. These calculations converged successfully with $R = 0.0331$ and $R' = 0.0238$ ($w \propto 1/\sigma^2$) using SHELX 76.[7] Least-squares planes and torsion angles were calculated using the program XANADU. Fractional atomic co-ordinates are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Analysis, Characterization, and Stability Constants.—The analytical and usual characterization techniques, as well as the experimental methods and computer programs used in the stability constant determinations, have been previously described.[3] In addition, differential scanning calorimetric (d.s.c.)

Table 4. Data obtained from non-isothermal thermogravimetric and d.s.c. measurements.

	Temperature range (°C)	Mass loss (%)	D.s.c. (kJ mol^{-1})
(*i*) $[Cu(pydca)(en)(H_2O)]\cdot H_2O \longrightarrow Cu(pydca)(en) + 2H_2O$	50—95	11.1 (11.1)	85
(*ii*) $[Cu(pydca)(pn)(H_2O)]\cdot H_2O \longrightarrow Cu(pydca)(pn) + 2H_2O$	40—70	10.0 (10.5)	52
(*iii*) $[Cu(pydca)(tmen)(H_2O)]\cdot H_2O \longrightarrow Cu(pydca)(tmen) + 2H_2O$	90—100	9.7 (9.5)	106
(*iv*) $[Cu(pydca)(pen)(H_2O)]\cdot H_2O \longrightarrow Cu(pydca)(pen) + 2H_2O$	50—75	8.3 (8.3)	69

measurements were made using a Perkin-Elmer DSC2 calorimeter. The empirical formulae of all the products obtained by thermogravimetric techniques were verified by C, H, and N analysis.

Results and Discussion

Analytical and magnetic data are given in Table 2. Data concerning pertinent bands in the electronic and i.r. spectra are summarized in Table 3.

The i.r. spectrum of $Cu(pydca)(en)\cdot 2H_2O$ contains single, relatively symmetrical $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ absorption bands at 1 630 and 1 380 cm^{-1}, respectively. The corresponding bands in the free ligand are at 1 700 and 1 360 cm^{-1}. The shifts in position, and the shapes of these bands, suggest that both carboxylate groups of pydca are co-ordinated, in a similar monodentate manner, to the copper atom.[8] The i.r. spectrum of H_2pydca has bands at 420 and 645 cm^{-1} which are ascribed to deformations in the pyridine ring. These bands are split and shifted to higher energy upon complex formation. This phenomenon is associated with pyridine co-ordination.[9] The presence of the two bands at 480 and 470 cm^{-1} is ascribed to co-ordination of both nitrogen atoms of en.[9] The co-ordination of a water molecule cannot be verified from the i.r. spectrum. However, the relatively low absorption coefficients for bands in the electronic spectrum of $Cu(pydca)(en)\cdot 2H_2O$ indicate a copper chromophore having octahedral symmetry. Since there is a good correlation between the solid reflectance and the solution spectra, the co-ordination number of $Cu(pydca)(en)\cdot 2H_2O$ must also be six. This can only be achieved by co-ordination of one of the water molecules. The complex can therefore best be formulated as $[Cu(pydca)(en)(H_2O)]\cdot H_2O$, the copper atom being in a distorted octahedral environment, consisting of one water and two carboxylate oxygen atoms, and one pyridine and two amine nitrogen atoms.

Analogous reasoning leads to the assignment of the formula $[Cu(pydca)(pn)(H_2O)]\cdot H_2O$, with copper in a similar distorted octahedral co-ordination sphere, for the corresponding $Cu(pydca)(pn)\cdot 2H_2O$ complex. The non-isothermal thermogravimetric and d.s.c. data, Table 4, for both complexes could not distinguish between the co-ordinated and lattice water molecules. These data show that the water in $[Cu(pydca)(en)(H_2O)]\cdot H_2O$ is more strongly bound than that in $[Cu(pydca)(pn)(H_2O)]\cdot H_2O$. The copper–water bond in the latter complex is therefore longer and the chromophore more tetragonally distorted. This is also reflected in the high absorption coefficients found for this compound.

The i.r. characterization data for the anhydrous complexes Cu(pydca)(en) and Cu(pydca)(pn) indicate identical monodentate co-ordination of the two carboxylate groups, as well as co-ordination of the pyridine and the amine nitrogen atoms. The solid reflectance electronic spectra differ compared to those of the corresponding hydrated complexes. Such differences would be consistent with a change in the symmetry of the chromophores from octahedral to five-co-ordinate. This assignment could be confirmed if the absorption coefficients of the bands were known. However, these could not be determined since the complexes were only sufficiently soluble for such measurements in aqueous alcohol mixtures. Nevertheless, the assignment of a distorted square-pyramidal stereochemistry to these complexes can be made with some confidence.

The characterization data of $Cu(pydca)(tmen)\cdot 2H_2O$ and $Cu(pydca)(pen)\cdot 2H_2O$ are ambiguous. The i.r. spectra contain split $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ absorption bands. These bands resemble the corresponding bands in $Cu(pydca)\cdot 2H_2O$. The pydca in this compound has one carboxylate group co-ordinated in the usual monodentate manner while an oxygen atom in the second group is co-ordinated to two copper atoms. However, the spectrum of the corresponding $Ni(pydca)(tmen)\cdot 2H_2O$ complex also exhibits split carboxylate bands.[4] An *X*-ray structure determination[4] shows the nickel to be in an octahedral environment consisting of one co-ordinated water molecule, bidentate co-ordinated tmen, and tridentate co-ordinated pydca. The bonding *via* the two carboxylate groups of pydca is monodentate and almost indistinguishable. Since the i.r. spectra of $Ni(pydca)(tmen)\cdot 2H_2O$ and $Cu(pydca)(tmen)\cdot 2H_2O$ are alike, similar bonding by pydca and tmen is postulated for the copper complex. The water molecules of $[Ni(pydca)(tmen)(H_2O)]\cdot H_2O$ were removed in two discrete steps whereas for the copper complex both were lost simultaneously and at a lower temperature. The energy required to remove the water molecules was 110 and 106 kJ mol^{-1} for the nickel and copper complexes, respectively. The relatively high absorption coefficients found for bands in the electronic spectrum of $Cu(pydca)(tmen)\cdot 2H_2O$ are consistent with a tetragonally distorted octahedral chromophore. The most plausible explanation for the above characterization data is a $[Cu(pydca)(tmen)(H_2O)]\cdot H_2O$ complex with copper in a tetragonally distorted octahedral environment, the distortion being produced by elongation of the Cu–O(water) and one Cu–N(amine) bond. A similar rationale led to the assignment of an analogous structure, with formula $[Cu(pydca)(pen)(H_2O)]\cdot H_2O$, to the corresponding pen complex. The absorption coefficients obtained from the electronic spectrum are even higher than those found for $[Cu(pydca)(tmen)(H_2O)]\cdot H_2O$. The greater steric hindrance associated with pen appears to increase the degree of distortion in the complex.

Interpretation of the characterization data for Cu(pydca)(tmen), Cu(pydca)(pen), and Cu(pydca)(tmpn) in an analogous manner to the above results in the assignment of five-co-ordinate environments for all the copper complexes. However, all have i.r. spectra exhibiting the anomalous split carboxylate bands. The fact that $Cu(pydca)\cdot 2H_2O$ achieves an octahedral co-ordination *via* oxygen bridging, and that this results in similar split carboxylate i.r. bands, brought doubt to this assignment. The complex Cu(pydca)(tmpn) was isolated in suitable crystalline form and a single crystal *X*-ray structure determination was successfully performed.

The asymmetric unit, with hydrogen atoms omitted, and showing the atomic numbering, is illustrated in the Figure. Selected bond lengths and angles are listed in Table 5, mean planes, torsion angles and selected contact distances are given in

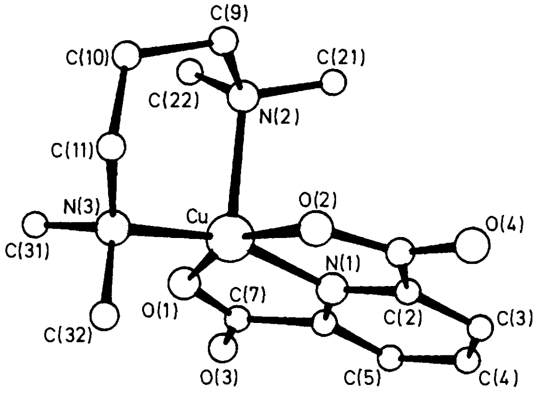

Figure. Molecular structure of [Cu(pydca)(tmpn)] and atomic numbering (hydrogen atoms omitted for clarity)

Table 5. Selected interatomic distances (Å) and angles (°), with standard deviations in parentheses

Cu–N(1)	1.915(2)	O(1)–Cu–O(2)	157.8(1)
Cu–O(1)	2.013(1)	N(1)–Cu–N(3)	158.0(1)
Cu–O(2)	2.041(1)	N(2)–Cu–O(1)	103.5(1)
Cu–N(3)	2.011(2)	N(2)–Cu–N(1)	105.5(1)
Cu–N(2)	2.255(2)	N(2)–Cu–O(2)	91.6(1)
		N(2)–Cu–N(3)	95.9(1)
C(7)–O(1)	1.292(2)	N(1)–Cu–O(1)	80.4(1)
C(8)–O(2)	1.289(2)	N(1)–Cu–O(2)	79.9(1)
C(7)–O(3)	1.228(2)	N(3)–Cu–O(1)	99.6(1)
C(8)–O(4)	1.227(2)	N(3)–Cu–O(2)	94.8(1)
N(1)–C(6)	1.333(2)		
N(1)–C(2)	1.337(2)	Cu–O(1)–C(7)	115.4(1)
C(5)–C(6)	1.383(3)	Cu–O(2)–C(8)	115.0(1)
C(2)–C(3)	1.381(3)	Cu–N(1)–C(6)	118.5(1)
C(3)–C(4)	1.396(3)	Cu–N(1)–C(2)	118.9(1)
C(5)–C(4)	1.393(3)	O(1)–C(7)–C(6)	114.1(2)
		O(2)–C(8)–C(2)	114.0(2)
N(2)–C(9)	1.484(3)	O(1)–C(7)–O(3)	126.0(2)
C(9)–C(10)	1.525(3)	O(2)–C(8)–O(4)	126.5(2)
C(10)–C(11)	1.519(3)	O(3)–C(7)–C(6)	119.9(2)
C(11)–N(3)	1.502(3)	O(4)–C(8)–C(2)	119.6(2)
N(2)–C(21)	1.476(3)		
N(2)–C(22)	1.483(3)	Cu–N(2)–C(9)	108.1(1)
N(3)–C(31)	1.487(3)	Cu–N(3)–C(11)	112.1(1)
N(3)–C(32)	1.498(3)		

Table 6. Least-squares planes (*a*), torsion angles (°) (*b*), and selected shorter contact distances (Å) (*c*)

(*a*)	Plane	Deviations from plane (Å)	R.m.s.d.(Å)
	1	N(1) (0.074), O(1) (−0.062), O(2) (−0.063), N(3) (0.051)	0.063
	2	N(1) (−0.017), C(2) (0.014), C(3) (0.000), C(4) (−0.010), C(5) (0.007), C(6) (0.006)	0.011
	3	C(6) (0.003), C(7) (−0.012), O(1) (0.004), O(3) (0.004)	0.007
	4	C(2) (0.001), C(8) (−0.004), O(2) (0.001), O(4) (0.001)	0.002

(*b*)	N(1)–C(2)–C(8)–O(2)	3.7
	N(1)–C(6)–C(7)–O(1)	1.3

(*c*)	O(1)···C(31)	3.07	O(2)···C(32)	3.26
	O(1)···H(313)	2.54	O(2)···H(321)	2.60
	O(3)···C(22)	3.42	O(4)···C(32)	3.38
	O(3)···H(222)	2.53	O(4)···H(322)	2.43
	O(1)···N(2)	3.36	O(2)···N(2)	3.08
	O(1)···N(3)	3.07	O(2)···N(3)	2.98

Table 6. The co-ordination sphere was shown to be five-co-ordinate with both carboxylate groups bonding in a similar monodentate manner. The environment of the copper atom can best be described as distorted square pyramidal, the basal plane [Table 6(*a*), plane 1] consisting of the three donor atoms O(1), O(2), and N(1) of pydca and N(3) of tmpn, while N(2) occupies the apical position. The Cu atom is elevated 0.308 Å above the basal plane. The apical Cu–N(2) bond length is considerably greater than the basal Cu–N(3) bond length. This tetragonal distortion is common in divalent copper complexes and is usually assumed to result from its d^9 electron configuration. However, a small degree of tetragonal distortion was also evident in [Ni(pydca)(tmen)(H$_2$O)]·H$_2$O.[4] This was ascribed to steric interaction between the methyl groups and the carboxylate oxygen atoms. Such interaction is also evident in Cu(pydca)(tmen); the O(1)···C(31) and O(2)···C(32) distances [Table 6(*c*)] are considerably smaller than 3.4 Å which is the sum of the van der Waals radii.[10] Therefore, the tetragonal distortion is probably due to both the electronic and steric factors.

The plane containing the Cu, N(2), and N(3) atoms does not bisect the pydca molecule. This greatly reduces the symmetry of the co-ordination sphere as indicated by the considerable differences in the N(2)–Cu–O(1) and N(2)–Cu–O(2) as well as the N(3)–Cu–O(1) and N(3)–Cu–O(2) angles. Both sets of angles should be identical in a symmetric structure. The O(1)···N(3), O(2)···N(2), and O(2)···N(3) distances are significantly less than the sum of the van der Waals radii for these atoms. Hence, there must be considerable steric interaction between these atoms. The distortion therefore appears to be the result of a process whereby the steric interactions, between the methylated amine and the carboxylated groups, are minimised.

The internal bonding in the two carboxylate groups is almost identical, equivalent bonds having the same lengths. The C–O (co-ordinated) bond lengths are longer than the C–O (unco-ordinated) bond lengths which is in agreement with the formation of a covalent bond between the anionic carboxylate oxygen atoms and copper. However, the two groups are not equivalent. The most obvious discrepancy is the significantly different Cu–O distances. Furthermore, the angles between the normals of the plane containing the pyridine ring [Table 6(*a*) plane 2] and the two planes containing the carboxylate groups [Table 6(*a*), planes 3 and 4] are 4.9 and 5.9°, respectively. The difference in planarity of the carboxylate groups with respect to the pyridine ring is better reflected in the magnitude of the torsion angles N(1)–C(2)–C(8)–O(2) and N(1)–C(6)–C(7)–O(2) [Table 6(*b*)]. It is reasonable to assume that if the magnitude of the steric interaction between the methylated amine groups and carboxylate groups is sufficiently large to cause gross distortions in the bonding of the amine ligand, it must be sufficient to account for the distortion in the carboxylate entities.

The splitting in the ν_{asym}(COO) and ν_{sym}(COO) i.r. bands can be rationalized by differences in the two carboxylate groups. These may be due to different metal–oxygen bond lengths or differences in the electronic properties. Rotation of the carboxylate group with respect to the pyridine ring will affect the degree of electron delocalization and therefore the carbon–oxygen bonds. The structural data, which show that both these phenomena are present in [Cu(pydca)(tmpn)], can readily account for the splitting. Furthermore, the fact that the distortions were attributed to the presence of methylated amine groups explains why these bands are found in all the complexes containing tertiary amine ligands isolated in this study. The

Table 7. Stability constants of diamine species in solution at a constant ionic strength of 0.2 mol dm^{-3}, with estimated standard deviations in parentheses

	log β			
Equilibrium	en	pn	tmen	pen
$H^+ + L \rightleftharpoons HL^+$	9.910(3)	10.518(0)	9.216(1)	9.810(3)
$2H^+ + L \rightleftharpoons H_2L^{2+}$	16.995(7)	19.296(8)	15.228(1)	16.656(6)
$Cu^{2+} + L \rightleftharpoons [Cu(L)]^{2+}$	10.499(7)	9.758(6)	7.324(3)	7.16(7)
$Cu^{2+} + 2L \rightleftharpoons [Cu(L)_2]^{2+}$	19.522(12)	17.069(18)		
$Cu^{2+} + pydca^{2-} + L \rightleftharpoons Cu(pydca)(L)$	18.26(1)	17.41(2)	16.10(1)	15.50(1)

	log β		log β
$H^+ + pydca^{2-} \rightleftharpoons Hpydca^-$	4.352(5)	$2H^+ + pydca^{2-} \rightleftharpoons H_2pydca$	6.394(8)
$Cu^{2+} + pydca^{2-} \rightleftharpoons Cu(pydca)$	9.24*	$Cu^{2+} + 2pydca^{2-} \rightleftharpoons [Cu(pydca)]^{2-}$	16.74*

* Values obtained from the literature[11] and corrected for ionic strength (P. W. Linden and K. Murray, *Talanta*, 1982, **29**, 377).

co-ordination spheres of the complexes Cu(pydca)(tmen) and Cu(pydca)(pen) are therefore assigned a five-co-ordinate symmetry similar to that of [Cu(pydca)(tmpn)].

The stability constants for the formation of the various species found in solutions of Cu^{2+}, pydca, and diamine were determined, Table 7. Although some of the formation constants have previously been reported[11] these were redetermined since any discrepancies due to different experimental methods leads to compounded errors in the stability constants for the Cu(pydca)(L) complexes. There is very good agreement between the redetermined constants and the literature[11] values. Divalent copper forms numerous stable hydroxo species which makes the determination of stability constants difficult. The formation of a precipitate made the determination of the stability constant for [Cu(pydca)(tmpn)] impossible.

The stability constant for $Cu(pen)^{2+}$, obtained from measurements made in a solution containing Cu^{2+}, pydca, and pen was 7.18(3). This is not significantly different from that obtained when no pydca was present, Table 7. The presence of pydca allows measurements to be made in solutions with higher pH, without precipitate formation. Hence, even though the estimated standard deviations for the stability constants of the copper–pen complexes are high, the constants appear to be meaningful. The formation constants for $Cu(tmen)^{2+}$ and $Cu(pen)^{2+}$ are very similar while that of the analogous copper–*N,N,N′,N′*-tetramethyl-1,3-diaminopropane complex is so low that it cannot be determined in aqueous solution. The steric hindrance at the co-ordination sphere caused by the four methylene groups in the pyrrolidine ring must therefore be considerably less than that of two ethyl groups. The variation in stability of the Cu(pydca)(L) complexes, where L = en, pn, tmen, or pen, can readily be rationalized in terms of increased steric hindrance (tmen, pen) and change in chelate ring size from a five-membered ring (en) to a less stable six-membered ring (pn). Nevertheless, all four complexes are shown to be sufficiently stable so that five-co-ordination can be achieved by removal of the solvent molecule from the co-ordination sphere. The steric hindrance inherent in tmpn resulting from the presence of both a six-membered chelate ring and four methyl groups prevents the occupation of the sixth co-ordination site of copper by a water molecule. The decrease in stability associated with the steric hindrance is sufficiently small to allow the isolation of the stable five-co-ordinate complex [Cu(pydca)(tmpn)] even when using a 50% water–ethanol mixture as solvent.

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