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Co-ordination behaviour of *N*-carboxymethylpseudoephedrine: crystal structures of seven-co-ordinated cadmium(II) and *fac*-*RS*-octahedral copper(II) complexes

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Co-ordination compounds of *N*-[2-hydroxy-1(*R*)-methyl-2(*R*)-phenylethyl]-*N*-methylglycine (*N*-carboxymethylpseudoephedrine, Hcpse) with copper(II), cobalt(II) and cadmium(II) have been prepared and characterised. Crystal structures of copper and cadmium complexes were obtained. In the compound $[Cu(cpse)_2]\cdot H_2O$, two cpse are co-ordinated in a tridentate mode giving place to a *fac-RS*-octahedral geometry. The monomeric compound $[Cd(cpse)_2(H_2O)]$ has an uncommon seven-co-ordinate geometry with one cpse bonded in a similar arrangement to that of the copper(II) compound, with an oxygen from the carboxylate group in an apical position. The second cpse molecule is co-ordinated with all three atoms in the equatorial plane, the remaining axial position of the distorted pentagonal bipyramid being occupied by a water molecule. As for the latter complex, the metal centre of $[Cd(cpse)Cl(H_2O)]\cdot H_2O\cdot dmso$ (dmso = dimethyl sulfoxide) presents a distorted pentagonal-bipyramidal geometry where the apical positions are occupied by a water molecule and a chloride ion. The tridentate cpse ligand lies in the equatorial plane and the co-ordination sphere is completed by a chelating carboxylic group from another cpse ligand. Each carboxylate group of cpse is bridging two different cadmium atoms, forming a zigzag chain in a polymeric structure.

Metal ions play a vital role in a vast number of widely differing biological processes. Most naturally occurring metal ions are bound to proteins. The question of the nature and extent of metal ion–protein interaction is therefore a most important one. It has been the subject of extensive work using amides, amino acids and small peptides as model compounds.[1–3] The binding of metal ions may control the conformation of biological molecules and so affect their chemical and biological properties. In this context we have been interested in the chemistry of co-ordination compounds derived from N-substituted glycine ligands which may act as tridentate molecules. Many tridentate ligands have a strong preference for facial or meridional co-ordination, for example some amino acids co-ordinate facially,[4,5] while glycylglycine co-ordinates meridionally,[6,7] or both geometries could be stabilised, as in the case of iminodiacetic acid derivatives.[8–13] *N*-(Phosphonomethyl)glycine may stabilise all possible geometric isomers;[14] once the nitrogen is attached to a metal atom its stereochemistry is fixed, adopting either an *R* or *S* configuration. It was found in previous works with some pseudoephedrine [2-(methylamino)-1-phenylpropan-1-ol] derivatives such as phenylboronic acids[15–18] and diorganotin(IV) oxides[19] that only one molecule of the ligand was facially co-ordinated to the Lewis acid, through the alkoxide, one carboxylic oxygen and the nitrogen, giving bicyclic compounds. The co-ordination behaviour of *N*-[2-hydroxy-1(*R*)-methyl-2(*R*)-phenylethyl]-*N*-methylglycine (*N*-carboxymethylpseudoephedrine, Hcpse) towards transition-metal ions has not been investigated, therefore we initiated a study of its complexing ability.

Experimental

Materials

Metal salts and solvents were obtained from E. Merck and J. T. Baker. All reagents were used without further purification.

Syntheses

***N*-[2-Hydroxy-1(*R*)-methyl-2(*R*)-phenylethyl]-*N*-methylglycine (Hcpse).** A mixture of (−)pseudoephedrine (5 g, 30.3 mmol), glyoxal (40% in water; 4.8 cm^3, 33.3 mmol), and EtOH (5 cm^3) was stirred at 70 °C for 16 h. The mixture was then evaporated *in vacuo* and the product recrystallised from EtOH–acetone; yield 5.35 g (80%), m.p. 153 °C.[20]

$[Cu(cpse)_2]\cdot H_2O$ 1. In a test-tube, Hcpse (0.0334 g, 0.15 mmol) was dissolved in EtOH (5 cm^3), and an aqueous solution (5 cm^3) of $Cu(O_2CMe)_2\cdot H_2O$ (0.0149 g, 0.075 mmol) was added slowly in order to obtain an interface between the two solvents. After 2 d blue needles were obtained at the interface. The crystals were filtered off, washed with methanol and dried *in vacuo*; yield 0.053 g (67.3%).

$[Cu(cpse)Br]$ 2, $[Cu(cpse)(NO_3)]$ 3 and $[Co(cpse)_2]\cdot 2H_2O$ 4. All these compounds were prepared using a 2 : 1 Hcpse : metal salt molar ratio. The metal salt (0.25 mmol) was dissolved in boiling MeOH (10 cm^3) and added to a hot solution of Hcpse (0.1116 g, 0.5 mmol) in MeOH (10 cm^3). The mixture was stirred for 1 h and then set aside at room temperature until a precipitate formed. The resulting precipitate was filtered off, washed and dried *in vacuo*; yields 0.0952 g (52.1), 0.0751 g (43.2) and 0.152 g (58.3%) for **2**, **3** and **4** respectively.

$[Cd(cpse)_2(H_2O)]$ 5. The metal salt $Cd(O_2CMe)_2\cdot 2H_2O$ (0.0765 g, 0.25 mmol) dissolved in boiling MeOH (10 cm^3) was added to a hot methanol solution (30 cm^3) of Hcpse (0.1116 g, 0.5 mmol). The reaction mixture was refluxed for 3 h. The white precipitate was filtered off, washed with methanol and dried *in vacuo*. Transparent crystals of compound **5** were obtained after 2 weeks from a solution of this precipitate dissolved in dimethyl sulfoxide (dmso); yield 0.0436 g (30.3%).

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Table 1 Elemental analyses for Hcpse and co-ordination compounds **1–8**

Compound	Colour	Analysis (%)* C	H	N
Hcpse	Cream	63.42 (64.54)	8.00 (7.67)	6.26 (6.27)
1 $[Cu(cpse)_2]\cdot H_2O$	Blue	54.22 (54.78)	6.39 (6.51)	5.40 (5.32)
2 $[Cu(cpse)Br]$	Blue-green	39.30 (39.41)	4.12 (4.13)	3.74 (3.83)
3 $[Cu(cpse)(NO_3)]$	Blue-green	42.55 (41.43)	4.95 (4.63)	8.09 (8.05)
4 $[Co(cpse)_2]\cdot 2H_2O$	Pink	54.00 (53.43)	7.05 (6.73)	4.72 (5.19)
5 $[Cd(cpse)_2(H_2O)]$	White	50.63 (49.95)	6.08 (6.28)	4.95 (4.85)
6 $[Cd(cpse)Cl(H_2O)]\cdot H_2O\cdot$dmso	White	35.55 (34.72)	4.91 (5.41)	3.29 (2.89)
7 $[Cd(cpse)Br(H_2O)]\cdot 2H_2O$	White	31.93 (30.75)	4.17 (4.73)	2.88 (2.98)
8 $[Cd(cpse)(NO_3)(H_2O)]\cdot H_2O$	White	34.00 (33.30)	4.53 (4.65)	6.36 (6.47)

* Calculated values in parentheses.

$[Cd(cpse)Cl(H_2O)]\cdot H_2O\cdot$dmso 6. In a test-tube, Hcpse (0.0610 g, 0.25 mmol) was dissolved in EtOH (5 cm^3), and an aqueous solution (5 cm^3) of $CdCl_2\cdot 2.5H_2O$ (0.0285 g, 0.125 mmol) was added slowly in order to obtain an interface between the two solvents. After 5 d a white precipitate was obtained in a very low yield, which was filtered off, washed with methanol and dried *in vacuo*. The microcrystals were soluble in dmso and single crystals of compound **6** were obtained after 4 months by slow evaporation of the solution.

$[Cd(cpse)Br(H_2O)]\cdot 2H_2O$ 7 and $[Cd(cpse)(NO_3)(H_2O)]\cdot H_2O$ 8. The corresponding metal salt (0.25 mmol) was dissolved in boiling MeOH (10 cm^3) and added to a hot solution of Hcpse (0.1116 g, 0.5 mmol) in MeOH (30 cm^3). The reaction mixture was refluxed for 2 h. The white precipitate was filtered off, washed with methanol and dried *in vacuo*; yields 0.075 g (64) and 0.0235 g (21.72%) for **7** and **8** respectively.

Physical measurements

Diffuse reflectance spectra were recorded on a Cary 5E UV/VIS/NIR spectrophotometer over the range 250–2500 nm, IR spectra on a Nicolet FT-IR 740 spectrophotometer using KBr pellets in the range 4000–400 cm^{-1} and polyethylene pellets in the range 700–70 cm^{-1} and ^{13}C (67.80 MHz) NMR spectra on a JEOL GSX-270 spectrometer. Magnetic susceptibility measurements of powdered samples were recorded on a Johnson Matthey balance using the Gouy method. Elemental analyses were performed by the Microanalytical Department, University College, London (see Table 1).

Crystallography

Suitable single crystals of $[Cu(cpse)_2]\cdot H_2O$ **1**, $[Cd(cpse)_2(H_2O)]$ **5** and $[Cd(cpse)Cl(H_2O)]\cdot H_2O\cdot$dmso **6** were obtained as described previously. In the case of **6** total decomposition of the crystal after 32 h of irradiation prevented the collection of data at high resolution ($\theta_{max} = 20°$) and an absorption correction. The diffraction data were collected at 293 K on a Siemens P4/PC automatic diffractometer using graphite-monochromatised Mo-Kα radiation ($\lambda = 0.710\,73$ Å) at variable scan speed in ω (4 to 60° min^{-1} for **1**, 2 to 30° min^{-1} for **5**, 3 to 60° min^{-1} for **6**) in the 2θ range of 4–50° for **1** and **5**, and 3–40° for **6**. Pertinent crystal data and other crystallographic parameters are listed in Table 2. The measured intensities were corrected for variation of check reflections monitored periodically (minimum 1.00, maximum 1.04, for **1** and **5**; 0.91, 1.00 for **6**) and Lorentz-polarisation effects. An absorption correction was not considered necessary in the case of compound **1** due to the needle shape of the crystal, but was applied for **5** which was a very thin plate, using 21 ψ scans with χ close to 90°, yielding minimum and maximum transmission factors of 0.227 and 0.246. Computations were performed with the SHELXTL [21] package on a personal computer and scattering factors were taken from ref. 22. The non centrosymmetric character of the space groups was confirmed by Wilson's statistics yielding $\langle|E^2 - 1|\rangle = 0.681$ for **1**, 0.653 for **5** and 0.676 for **6**.

The structure of compound **1** was solved by direct methods followed by subsequent Fourier-difference maps and refined by full-matrix least squares, minimising $\Sigma[w(F_o - F_c)^2]$, without restraints or constraints. Hydrogen atoms attached to carbon atoms were included at geometrically idealised positions and refined using a riding model with fixed isotropic U. For the two hydroxyl groups [O(4) and O(7)] and the water molecule [O(1)], hydrogen atoms could not be positioned from a Fourier-difference map and were omitted. The correct absolute configuration of the molecule was confirmed by refinement of a Rogers parameter:[23] $\eta = 0.97(6)$.

The solution for compound **5** was derived from the interpretation of the Patterson map completed and refined as for **1**. The hydrogen atoms of the water molecule O(1) and of the hydroxyl groups O(4) and O(7) were omitted and the remaining hydrogen atoms were treated as for **1**. The correct absolute configuration was confirmed in the same way, giving $\eta = 0.98(15)$.

The molecular structure of compound **6** was resolved and refined as for **1**. The hydrogen atoms of the water molecules O(1) and O(7) as well as for the hydroxyl group O(4) were omitted. The absolute configuration was confirmed from refinement of the Rogers parameter $\eta = 1.2(2)$. The solvent molecules were refined with isotropic thermal parameters because of lack of data.

No significant features were observed in the last Fourier-difference maps for compounds **1** and **5**. In case of **6** the largest residual peak (2.26 e Å^{-3}) was close to S(1) from the dmso solvent molecule.

CCDC reference number 186/644.

Results and Discussion

The reaction of Hcpse with copper(II), cobalt(II) and cadmium(II) afforded two types of compounds, which are summarised in Table 1. When using their acetate salts in the synthesis, two cpse molecules are co-ordinated. In complexes

Table 2 Crystallographic data for compounds **1**, **5** and **6**

	1	**5**	**6**
Formula	$C_{24}H_{32}CuN_2O_6\cdot H_2O$	$C_{24}H_{34}CdN_2O_7$	$C_{12}H_{18}CdClNO_4\cdot H_2O\cdot(CH_3)_2SO$
M	526.07	574.93	484.27
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
a/Å	6.271(2)	14.717(4)	8.194(1)
b/Å	13.598(3)	6.279(2)	12.467(1)
c/Å	28.721(6)	15.618(4)	19.795(3)
β/°		116.80(1)	
U/Å^3	2448.9(12)	1288.4(7)	2022.2(4)
Z	4	2	4
D_c/Mg m^{-3}	1.427	1.482	1.591
F(000)	1108	592	984
μ(Mo-Kα)/mm^{-1}	0.94	0.89	1.34
Crystal dimensions/mm	0.7 × 0.1 × 0.1	0.8 × 0.1 × 0.02	0.4 × 0.2 × 0.1
Total reflections measured	3369	3342	1578
No. unique reflections	3111	2945	1408
No. observed reflections [$F > 4\sigma(F)$]	2301	2225	1315
No. variables	308	308	194
Goodness of fit	0.90	1.06	2.25
$R = \Sigma(\lvert F_o - F_c\rvert)/\Sigma\lvert F_o\rvert$	0.049	0.046	0.046
$R' = \Sigma(w^{\frac{1}{2}}\lvert F_o - F_c\rvert)/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.059[a]	0.045[b]	0.065[c]

[a] $w = [\sigma^2(F) + 0.0021F^2]^{-1}$. [b] $w = [\sigma^2(F) + 0.0003F^2]^{-1}$. [c] $w = [\sigma^2(F) + 0.0004F^2]^{-1}$.

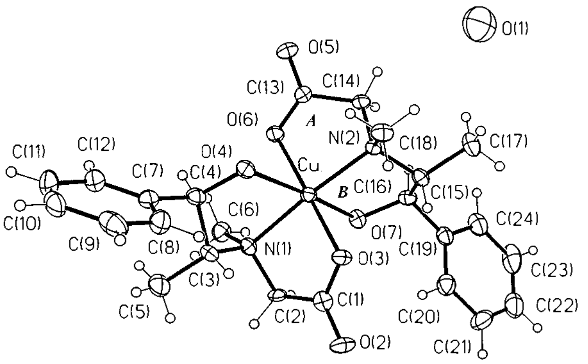


Fig. 1 Geometry and atom numbering for $[Cu(cpse)_2]\cdot H_2O$ **1**

Table 3 Selected bond lengths (Å) and angles (°) with standard deviations in parentheses for compound **1**

Cu–O(7)	2.379(5)	Cu–O(4)	2.475(5)
Cu–O(3)	1.974(5)	Cu–O(6)	1.944(5)
Cu–N(1)	2.048(6)	Cu–N(2)	2.030(6)
O(3)–C(1)	1.296(8)	O(2)–C(1)	1.216(9)
O(4)–C(4)	1.434(8)	N(1)–C(2)	1.476(9)
N(1)–C(3)	1.520(10)	N(1)–C(6)	1.470(10)
C(1)–C(2)	1.508(10)	C(3)–C(4)	1.545(9)
C(3)–C(5)	1.526(10)	C(4)–C(7)	1.530(11)
O(4) · · · O(5)*	2.626	O(2) · · · O(7)*	2.599
O(4)–Cu–O(7)	175.4(2)	O(3)–Cu–O(4)	95.8(2)
O(6)–Cu–O(7)	98.4(2)	O(3)–Cu–O(7)	85.7(2)
O(4)–Cu–O(6)	80.1(2)	O(3)–Cu–O(6)	175.7(2)
N(1)–Cu–N(2)	173.1(2)	N(1)–Cu–O(3)	83.2(2)
N(1)–Cu–O(4)	79.5(2)	N(1)–Cu–O(6)	97.2(2)
N(1)–Cu–O(7)	96.4(2)	N(2)–Cu–O(3)	94.8(2)
N(2)–Cu–O(4)	107.4(2)	N(2)–Cu–O(7)	76.8(2)
N(2)–Cu–O(6)	85.3(2)	Cu–O(3)–C(1)	111.6(4)
Cu–O(6)–C(13)	113.8(4)	Cu–O(4)–C(4)	101.9(4)
Cu–O(7)–C(16)	109.4(4)	Cu–N(1)–C(2)	101.2(4)
Cu–N(2)–C(14)	106.8(4)	Cu–N(2)–C(15)	110.1(4)
Cu–N(1)–C(3)	111.9(4)	Cu–N(2)–C(18)	105.9(4)
Cu–N(1)–C(6)	111.4(5)	O(6)–C(13)–C(14)	116.7(6)
O(3)–C(1)–C(2)	116.5(6)	N(2)–C(15)–C(16)	110.4(6)
N(1)–C(3)–C(4)	109.8(6)	C(16)–C(15)–C(17)	110.6(6)
C(4)–C(3)–C(5)	112.8(6)		

* Intermolecular oxygen–oxygen contact for hydrogen bonds.

obtained from copper(II) and cadmium(II) chloride, bromide or nitrate the metal ion is co-ordinated to only one cpse molecule and to a counter ion.

Crystal structures of compounds 1, 5 and 6

A perspective view of complex $[Cu(cpse)_2]\cdot H_2O$ **1**, with the labelling of the atoms is given in Fig. 1. The bond lengths and angles are listed in Table 3. Two cpse molecules are co-ordinated to the metal in a tridentate mode giving a bicyclic chelate with two distorted five-membered rings, where the nitrogen and the oxygens from the carboxylic and the alkoxide functions are bonded to the metal ion. The compound presents a *fac-RS*-octahedral geometry with the copper(II) ion in the centre bonded to the six atoms in an all-*trans* configuration. The carbonyl rings have distances Cu–O(3) and Cu–O(6) of 1.974(5) and 1.944(5) Å, respectively. The Cu–N(1) 2.048(6) and Cu–N(2) 2.030(6) Å distances are very similar to those observed in an analogous five-membered ring of a copper(II) monoethyliminodiacetato complex;[8] on the other hand, the Cu–O bond lengths in the axial positions are different from each other, Cu–O(4) 2.475(5) and Cu–O(7) 2.379(5) Å, due to a Jahn–Teller effect. The two C–O distances in the carboxylate group are very similar (Table 3), due to the presence of hydrogen bonding in the network structure between the non-co-ordinated O(2, 5) and the H(4, 7) from neighbouring molecules, as has been observed in other systems.[5]

The cadmium compound **5** has an uncommon seven-co-ordinate geometry (Fig. 2). Up to now just a few examples for this type of co-ordination are known, mainly in polymeric complexes.[24–26] Selected bond lengths and angles are listed in Table 4. The geometry can be regarded as distorted pentagonal bipyramidal with one cpse ligand bonded to the metal ion in a similar arrangement to that of the copper(II) compound, with an oxygen from the carboxylate group in an apical position, Cd–O(6) 2.301(8) Å, and the nitrogen and the alkoxide oxygen in the equatorial plane, Cd–N(2) 2.448(9) and Cd–O(7) 2.341(5) Å. The second cpse molecule is co-ordinated with all three atoms in the equatorial plane, an unusual co-ordination mode for this ligand, Cd–O(3) 2.368(8), Cd–N(1) 2.398(7) and Cd–O(4) 2.534(6) Å; these distances are similar to normal Cd–O and Cd–N bonds,[24–26] with exception of Cd–O(4) which is longer than expected, probably due to steric hindrance from the methyl group of the A ring of the other ligand, as can be appreciated from the small angle N(1)–Cd–O(4) 67.7(3)°, which is substantially smaller than the corresponding one of complex **1**, 79.5(2)°. The seventh position is occupied by a water mole-

Table 4 Selected bond lengths (Å) and angles (°) with standard deviations in parentheses for compound **5**

Cd–O(1)	2.318(8)	Cd–O(4)	2.534(6)
Cd–O(3)	2.368(8)	Cd–O(6)	2.301(8)
Cd–O(7)	2.341(5)	Cd–N(1)	2.398(7)
Cd–N(2)	2.448(9)	O(2)–C(1)	1.209(16)
O(3)–C(1)	1.261(14)	O(5)–C(13)	1.228(13)
O(6)–C(13)	1.261(15)	N(1)–C(2)	1.451(27)
N(2)–C(14)	1.471(13)	N(1)–C(3)	1.490(9)
N(2)–C(15)	1.493(14)	C(1)–C(2)	1.557(16)
C(13)–C(14)	1.524(17)	O(4) ··· O(5)*	2.606
O(1)–Cd–O(6)	172.2(3)	O(1)–Cd–O(4)	87.8(2)
O(1)–Cd–O(3)	95.6(3)	O(1)–Cd–O(7)	85.2(2)
N(1)–Cd–O(1)	99.3(5)	N(2)–Cd–O(1)	100.8(4)
N(1)–Cd–N(2)	138.9(2)	N(1)–Cd–O(3)	70.8(3)
N(1)–Cd–O(4)	67.7(3)	N(1)–Cd–O(6)	86.6(5)
O(3)–Cd–O(7)	75.3(2)	N(2)–Cd–O(7)	71.3(2)

* Intermolecular oxygen–oxygen contact for hydrogen bonds.

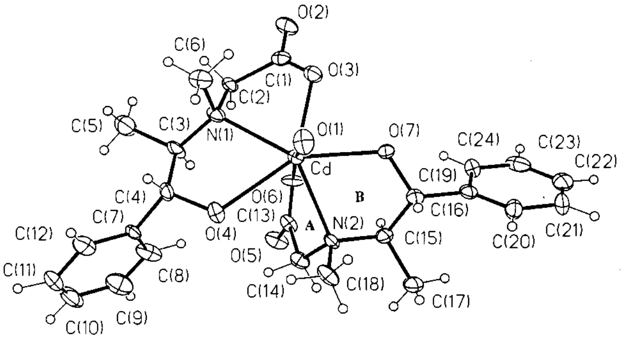


Fig. 2 Geometry and atom numbering for $[Cd(cpse)_2(H_2O)]$ **5**

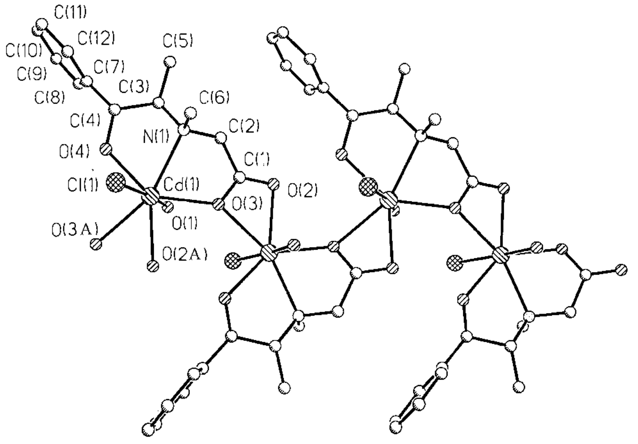


Fig. 3 Geometry of the polymeric part of $[Cd(cpse)Cl(H_2O)]\cdot H_2O\cdot dmso$ **6**

cule, Cd–O(1) 2.318(8) Å, with a typical bond length for apical co-ordination.[24–26]

As for the previous complex **5**, the metal centre of **6** has a seven-co-ordinated environment with a distorted pentagonal-bipyramidal geometry (see Table 5). The apical positions are occupied by a water molecule and a chloride ion, Cl–Cd–O(1) 169.6(3)°. As observed in **5**, the tridentate cpse ligand lies in the equatorial plane, Cd–O(3) 2.323(9), Cd–N(1) 2.437(12) and Cd–O(4) 2.360(10) Å, however the co-ordination sphere is completed by a chelated carboxylic group from another cpse ligand, Cd–O(2A) 2.410(11) and Cd–O(3A) 2.500(10) Å. Each carboxylate group of cpse is bridging two different cadmium atoms, as in $Cd(O_2CMe)_2(H_2O)_2$,[27] forming a zigzag chain structure as depicted in Fig. 3. Atoms Cd–O(3)–N(1)–O(4)–O(2A)–O(3A) all lie close to a plane with a maximum deviation of 0.23 Å for O(3). The shorter distance Cd–O(4) and the larger angle, N(1)–Cd–O(4) 72.7(4)°, when compared to those of compound **5**, indicate that there is no significant steric hindrance in this compound: this difference between the two complexes can be understood as a consequence of the atom which occupies an apical position in **5** and **6**, cpse carboxylate O(4) and a chloride ion, respectively.

Table 5 Selected bond lengths (Å) and angles (°) with standard deviations in parentheses for compound **6**

Cd(1)–Cl(1)	2.551(4)	Cd(1)–O(1)	2.336(10)
Cd(1)–O(3)	2.323(9)	Cd(1)–O(4)	2.360(10)
Cd(1)–O(2A)	2.410(11)	Cd(1)–O(3A)	2.500(10)
Cd(1)–N(1)	2.437(12)	O(2)–C(1)	1.259(20)
O(3)–C(1)	1.287(18)	O(4)–C(4)	1.406(19)
N(1)–C(6)	1.456(21)	N(1)–C(2)	1.447(20)
N(1)–C(3)	1.522(19)	O(2)–Cd(1A)	2.410(11)
O(3)–Cd(1A)	2.500(10)		
Cl(1)–Cd(1)–O(4)	87.4(3)	Cl(1)–Cd(1)–O(2A)	92.9(3)
Cl(1)–Cd(1)–O(2A)	92.9(3)	Cl(1)–Cd(1)–O(1)	169.6(3)
Cl(1)–Cd(1)–O(3)	109.7(4)	Cl(1)–Cd(1)–O(3A)	87.9(2)
N(1)–Cd(1)–O(3)	69.9(4)	N(1)–Cd(1)–O(4)	72.7(4)
O(3)–Cd(1)–O(2A)	80.23	O(4)–Cd(1)–O(3A)	83.6(3)
Cl(1)–Cd(1)–N(1)	92.7(3)		

Symmetry operation implied by A label: $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$.

The observed polymeric structure is very similar to that reported for triaqua(malonato)cadmium(II),[26] where the co-ordination sphere is comprised only of oxygen atoms. The structure of **6** is completed with a dmso and a water solvent molecule which form a complicated three-dimensional network by weak hydrogen-bond interactions with the polymeric system.

Spectroscopic characterisation of compounds 1–8

Some spectral and magnetic data of the co-ordination compounds of cpse are presented in Table 6. The IR spectrum of Hcpse shows bands of the ν_{asym} and ν_{sym} stretching modes of the carboxylic group at 1638 and 1384 cm^{-1}, whereas for compounds **1**–**5** these bands are shifted, presenting a $\Delta\nu(\nu_{asym} - \nu_{sym})$ of ≈200 cm^{-1}, which is in accordance with the inequivalence of the two C–O bonds in the carboxylic group.[28,29] This can be seen from the molecular structures of **1** and **5** (Tables 3 and 4; Figs. 1 and 2) where the C–O distance is longer for the oxygen bonded to the metal ion while the other presents more double-bond character. Owing to the similarity of the IR spectra of compounds **1**–**5**, it can be proposed that the ligand is co-ordinated in a monomeric tridentate mode. Additionally, the copper compound **3** showed new bands from a co-ordinated nitrate group (1344 and 1318 cm^{-1}) and the far-IR spectrum of compound **2** has a strong band at 172 cm^{-1} assigned to ν(Cu–Br).[30]

The IR spectra of the cadmium(II) compounds **6**–**8** (Table 6) showed a Δν of ≈160 cm^{-1}, which has been observed for structures where chelation and monoatomic bridging[27,29] is present, as in compound **6**, Fig. 3. In the low-frequency infrared spectra of **6** and **7** the vibrational bands at 240 and 196 cm^{-1} were assigned as ν(Cd–Cl) and ν(Cd–Br) respectively.[30] Compound **8** presented new absorption bands due to a co-ordinated nitrate group (Table 6).

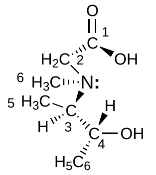
The reflectance spectrum of the crystalline compound **1** (Fig. 4) presents a band indicative of a tetragonally distorted octahedral geometry at 16357 cm^{-1} and the spectra of $[Cu(cpse)Br]$ **2** and $[Cu(cpse)(NO_3)]$ **3** (Fig. 4) exhibit a strong band (11848 and 12771 cm^{-1} respectively) in the region expected for a distorted tetrahedral geometry in copper(II) compounds.[31–38] This geometry could be stabilised by the tridentate cpse co-ordination, as shown in copper compound **1**, allowing the

Table 6 Spectral and magnetic data for compounds Hcpse and compounds **1**–**8**

Compound	$\mu_{eff}{}^{a}/\mu_B$	UV/VIS ^{b} λ_{max}/cm^{-1}	IR $^{c}\tilde{\nu}_{max}/cm^{-1}$ $\nu_{asym}(CO_2^-)$	$\nu_{sym}(CO_2^-)$	$\Delta\nu$	$\nu(M-X)$	$\nu(NO_3)$
Hcpse	—	—	1638	1384	253	—	—
1	2.16	16357	1633	1401	232	—	—
2	1.70	11848	1598	1403	195	ν_3 172	—
3	1.86	12771	1602	1385	217	—	ν_5 1344 ν_1 1318
4	5.19	ν_1 9183 ν_3 20325	1592	1408	212	—	—
5			1598	1398	200		
6	—	—	1569	1412	157	ν_3 240	—
7	—	—	1567	1410	157	ν_3 196	—
8	—	—	1565	1401	164	—	ν_5 1385 ν_1 1312

[a] 25 °C; $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}. [b] Diffuse reflectance. [c] From KBr pellets, in the range 4000–600 cm^{-1}, and polyethylene pellets, in the range 700–70 cm^{-1}.

Table 7 Carbon-13 NMR data for compounds Hcpse and compound **7** in $(CD_3)_2SO$



Carbon	δ Hcpse	**7**
1	167.1	173.9
2	56.1	62.6
3	65.1	72.7
4	72.2	79.2
5	9.8	7.9
6	36.9	40.7
i	141.4	141.8
o	127.4	128.1
m	128.4	127.8
p	128.2	127.6

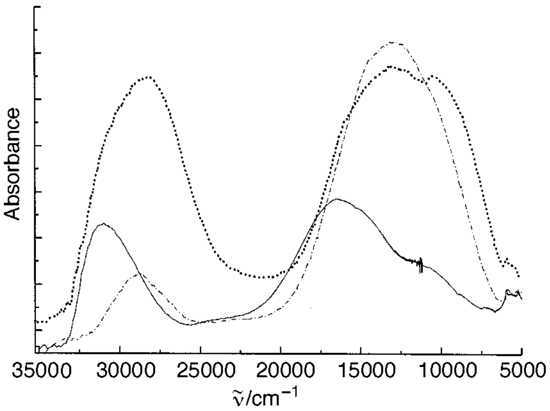


Fig. 4 Diffuse reflectance spectra of copper(II) compounds **1** (—), **2** (. . .) and **3** (–•–)

fourth position to be occupied by the anion. Nevertheless, there is a possibility that the cpse ligand may behave as a bridging ligand using the carboxylate functionality as in complex **6** or in **3** the nitrate could be bidentate. Their magnetic moments are as expected for a copper(II) ion.

The cobalt(II) compound **4** has a magnetic moment and diffuse electronic spectrum characteristic of a high-spin octahedral geometry with the transitions ν_1 $^4T_{2g}(F) \longleftarrow {}^4T_{1g}(F)$ at 9183 cm^{-1} and ν_3 $^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$ at 20325 cm^{-1}.

Cadmium(II) compound **7** is very soluble in dmso and its ^{13}C NMR spectrum was recorded (Table 7). Only one isomer was observed, although in principle two diastereomers may be expected. Comparison of the ^{13}C data between free Hcpse and complex **7** shows that the C(1) from the carboxylate group is shifted to lower magnetic field (Δδ 6.8 ppm). This is attributed to the co-ordination of the carboxylic oxygen to the metal ion. The same behaviour is observed for signals C(2) (Δδ 6.5 ppm) and C(3) (Δδ 7.6 ppm) indicating that the nitrogen atom is bonded to cadmium(II); also the low-field shift of C(4) (Δδ 7.0 ppm) shows that the OH group is co-ordinated.

In conclusion, the cpse molecule behaves as a tridentate ligand stabilising facial or meridional geometries. When acetate metal salts are employed in the synthesis co-ordination compounds with two cpse ligands bonded to the metal ions are obtained, whereas with chloride, bromide or nitrate salts only one ligand and one anion are co-ordinated. The carboxylate exhibited two types of co-ordination modes, being unidentate in monomeric compounds and bidentate (chelate) with monoatomic bridging in polymeric complexes. Interestingly, for the two cadmium(II) seven-co-ordinated compounds both co-ordination types were observed.

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References

1 S. H. Laurie, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1st edn., 1987, vol. 2, ch. 20.2, pp. 739–776.
2 S. J. Higgins, *Coord. Chem. Rev.*, 1996, **152**, 175.
3 P. A. Vigato, S. Tamburini and D. E. Fenton, *Coord. Chem. Rev.*, 1990, **106**, 25.
4 S. T. Chow and C. A. McAuliffe, *Prog. Inorg. Chem.*, 1975, **19**, 51.
5 P. E. Hoggard, *Inorg. Chem.*, 1981, **20**, 415.
6 V. Subramaniam and P. E. Hoggard, *Inorg. Chim. Acta*, 1989, **155**, 161.
7 V. Subramaniam, K.-W. Lee, R. G. Garvey and P. E. Hoggard, *Polyhedron*, 1988, **7**, 523.
8 J. A. Guevara García, N. Barba-Behrens, A. R. Tapia Benavides, M. J. Rosales-Hoz and R. Contreras, *Inorg. Chim. Acta*, 1995, **239**, 93.
9 V. Subramaniam, K.-W. Lee and P. E. Hoggard, *Inorg. Chim. Acta*, 1994, **216**, 155.
10 A. Castiñeiras Campos, A. Busnot, M. E. Abarca García, A. G. Sicilia Zafra, J. M. González and J. Niclós Gutiérrez, *Inorg. Chim. Acta*, 1994, **215**, 73.

11 N.-H. Dung, B. Viossat, A. Busnot, J. M. González, J. Niclós Gutiérrez and F. Gardette, *Inorg. Chim. Acta*, 1990, **174**, 145.
12 J. Niclós Gutiérrez, M. E. Abarca García, B. Viossat, N.-H. Dung, A. Busnot and J. F. Hemidy, *Acta Crystallogr., Sect. C*, 1993, **49**, 19.
13 L. Beyer, G. Kühn and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1965, **339**, 8.
14 D. Heineke, S. J. Franklin and K. N. Raymond, *Inorg. Chem.*, 1994, **33**, 2413.
15 N. Farfán, T. Mancilla, D. Castillo, G. Uribe, L. Carrillo, P. Joseph-Nathan and R. Contreras, *J. Organomet. Chem.*, 1990, **381**, 1.
16 L. Cuellar and R. Contreras, *J. Organomet. Chem.*, 1987, **321**, 191.
17 N. Farfán, P. Joseph-Nathan, L. M. Chiquete and R. Contreras, *J. Organomet. Chem.*, 1988, **348**, 149.
18 T. Mancilla, R. Contreras and B. Wrackmeyer, *J. Organomet. Chem.*, 1986, **307**, 1.
19 T. Mancilla and L. Carrillo, *Main Group Metal Chem.*, 1994, **17**, 363.
20 N. Farfán, L. Cuellar, J. M. Aceves and R. Contreras, *Synthesis*, 1987, 927.
21 G. M. Sheldrick, SHELXTL 4.2/360, Crystallographic Computing System, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
22 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
23 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.
24 M. L. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1974, 1922.
25 M. Fujita, Y. J. Kwon, M. Miyazawa and K. Ogura, *J. Chem. Soc., Chem. Commun.*, 1994, 1977.
26 K. H. Chung, E. Hong, Y. Do and C. H. Moon, *J. Chem. Soc., Dalton Trans.*, 1996, 3363.
27 W. Harrison and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1972, 956.
28 C. Oldham, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1st edn., 1987, vol. 2, ch. 15, pp. 435–459.
29 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
30 K. Nakamoto, *Infrared and Raman Spectra of Inorganic Coordination Compounds*, Wiley, New York, 4th edn., 1986.
31 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, 2nd edn., 1984, pp. 555–572.
32 B. F. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1st edn., 1987, vol. 5, ch. 53, pp. 533–774.
33 N. Barba-Behrens, A. Vazquez-Olmos, S. E. Castillo-Blum, G. Höjer, S. Meza-Höjer, R. M. Hernández, M. J. Rosales-Hoz, R. Vicente and A. Escuer, *Transition Met. Chem.*, 1996, **21**, 31.
34 S. Knapp, T. P. Keenan, X. Zhang, R. Fikar, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.*, 1990, **112**, 3452.
35 S. R. Desjardins, K. W. Penfield, S. L. Cohen, R. L. Musselman and E. I. Solomon, *J. Am. Chem. Soc.*, 1983, **105**, 4590.
36 E. Bernarducci, W. F. Schwindinger, J. L. Hughey, K. Krogh-Jespersen and H. J. Schugar, *J. Am. Chem. Soc.*, 1981, **103**, 1691.
37 R. J. Dudley, B. J. Hathaway and P. G. Hodgson, *J. Chem. Soc., Dalton Trans.*, 1972, 882.
38 E. M. Gouge and J. F. Geldard, *Inorg. Chem.*, 1978, **17**, 270.

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