REACTION OF THE BIHETEROAROMATIC LIGAND 2-(2'-PYRIDYL)QUINOXALINE (L) WITH ZINC(II) AND CADMIUM(II) HALIDES: PREPARATION AND CHARACTERIZATION OF THE 1:1 COMPLEXES

SPYROS P. PERLEPES

Department of Chemistry, University of Patras, 26500 Patra, Greece

SPYRIDOULA KASSELOURI and ACHILLEAS GAROUFIS

Department of Chemistry, Physics and Materials Technology, Technological Institution of Athens, Egaleo, Athens, Greece

FRANK LUTZ and ROBERT BAU

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0744, U.S.A.

and

NICK HADJILIADIS*

Laboratory of Inorganic and General Chemistry, Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece

Abstract—The reactions of ZnX_2 and CdX_2 (X = Cl, Br, I) with the biheteroaromatic ligand 2-(2'-pyridyl)quinoxaline (L) were studied in ethanolic solutions. The new complexes $[ZnX_2L]$ (X = Cl, Br, I), $[CdI_2L]$ and $[Cd_2X_4L_2]$ were isolated and characterized by elemental analyses, conductivity measurements, X-ray powder patterns, thermal methods (TG/DTG, DTA) and spectroscopic (IR, far-IR, Raman, ^1H NMR) studies. The X-ray crystal structure of $[ZnCl_2L] \cdot 0.5MeOH$ shows a distorted tetrahedral geometry around the zinc(II) atom. The ligand L acts as a bidentate chelate with the ligated atoms being the pyridine nitrogen and one of the quinoxaline nitrogens. A monomeric pseudo-tetrahedral structure is also assigned for $[ZnBr_2]$ and $[MI_2L]$ (M = Zn, Cd). Dimeric structures are proposed for the chloro and bromo cadmium(II) compounds, in which the two metal centres are bridged by two halo ligands, with a terminal halide and a chelating molecule of L completing five-coordination at each metal. All data are discussed in terms of the nature of bonding and known and assigned structures. A complex with the empirical formula Cd_2Cl_4L was isolated during the thermal decomposition of $[Cd_2Cl_4L_2]$; the vibrational study of this thermally stable intermediate shows that L acts as a tridentate bridging ligand. The crystal structure of $[Hg_2Br_4L_2]$, which was not available when the results of the HgX_2/L chemistry had been published, is also described.

2,2-Bipyridine (bpy) and 1,10-phenanthroline (phen) have been extensively used as ligands in both analytical and preparative coordination chem-

istry.[1,2] It is only relatively recently, however, that systematic studies of substituted derivatives of bpy, phen and other α-diimines have been undertaken;[3,4] as examples, recent reports demonstrate that these ligand systems have now been incorporated into macrocycles.[5,6] Much of this work has been initiated

---

* Author to whom correspondence should be addressed.

by the intense current interest in the catalytic, redox and photoredox properties of these ligands with various metals, particularly ruthenium.[7,8] The key feature of these nitrogen heterocycles containing six-membered rings is their π-electron deficiency, making them very good π acceptors; thus, they have been used to stabilize various metal complexes in lower oxidation states.[2,3] Although substituents on the pyridine rings can significantly modify the physical and chemical properties of complexes containing bpy ligands, much greater changes can result from the replacement of one, or both, of the pyridine rings by other nitrogen-containing heterocycles.[3] Such changes are explained by the very different electronic properties of the various nitrogen heterocycles.[9]

Of particular interest are binucleating ligands which have two non-equivalent sites for metal coordination. Such ligands offer great potential, particularly for the synthesis of heteronuclear complexes, since different metals can selectively complex at the different coordination sites.[10] A survey of the literature indicates that scarcely any data are available on such systems.[10] One molecule belonging to this family of ligands is 2-(2'-pyridyl)quinoxaline (L). Ligand L may combine the chelating properties of bpy[1,2] with the bridging properties of quinoxaline.[11]

The novel ligand 2-(2'-pyridyl)quinoxaline was derived unexpectedly from the unusual cyclization reaction between 1,2-phenylenediamine and 2-acetylpyridine.[12] In recent papers,[13–15] we reported that reactions of $CuCl_2$[13,14] and HgX_2[15] with one equivalent of L led to the isolation of products with the empirical formulae $CuCl_2L$ and HgX_2L, respectively. Single-crystal X-ray examination showed the 1 : 1 chloro compounds to be dinuclear $[M_2Cl_4L_2]$ species; the structure consists of two metal centres bridged by two chloro ligands, with a terminal chloride and a chelating molecule of L completing five-coordinations at each metal. At this point, we wondered whether a monomeric, 1 : 1 halide adduct could be prepared and structurally characterized. Zinc(II) was the metal chosen because of its tendency to give tetrahedral complexes.[16] We also wondered whether appropriate modification of the MX_2/L reaction systems, i.e. low L : MX_2 ratios, might instead yield clusters/polymers in which L would be capable of acting as a tridentate bridging ligand with mixed bidentate–monodentate coordination; recent Extended Huckel Molecular Orbital (EHMO) calculations[14] have shown that all three nitrogens of L are strong nucleophilic centres. Cadmium(II) was the metal chosen for this due to its well-known tendency to yield polymeric complexes with coordination numbers of 5 and 6.[16,17]

The current status of our work has established that only the first of the above objectives can be synthetically fulfilled. In this report, we describe the identity of the products obtained from the 1 : 1 and 2 : 1 MX_2/L reaction (M = Zn, Cd; X = Cl, Br, I) and their characterization with a number of techniques; the complex $[ZnCl_2L] \cdot 0.5MeOH$ has been structurally characterized by X-ray crystallography. In addition, we report the single-crystal X-ray structure of $[Hg_2Br_4L_2]$, which was not available when we submitted[15] the results of the HgX_2/L chemistry.

EXPERIMENTAL

General

All manipulations were performed under aerobic conditions using materials as received. The metal salts ZnX_2 (X = Cl, Br, I), $CdCl_2 \cdot 2H_2O$ and CdX_2 (X = Br, I) were used as starting materials. L and $[Hg_2Br_4L_2]$ were synthesized as described recently.[12,15] Metal and halide analyses were carried out using standard gravimetric and potentiometric methods. Microanalyses were performed by the University of Dortmund (Germany) Microanalytical Laboratory. Physicochemical measurements and spectroscopic techniques were carried out by published methods.[15,18,19]

Compound preparation

The metal complexes $[ZnX_2L]$ (X = Cl, Br, I), $[Cd_2Br_4L_2]$ and $[CdI_2L]$ were all prepared similarly. To a solution containing 0.7 mmol of the required anhydrous metal in absolute ethanol (6 cm³) was added dropwise a warm solution of L (0.7 mmol) in the same solvent (10 cm³). The resulting solutions were stirred at room temperature for 2 h. Solid products were deposited during this time, which were collected by filtration, washed with cold ethanol (5 cm³) and diethyl ether (3 × 5 cm³) and dried in vacuo over silica gel. For the preparation of $[Cd_2Cl_4L_2]$, to a solution of $CdCl_2 \cdot 2H_2O$ (0.7 mmol) in ethanol (17 cm³) was added triethyl ortho-formate (2 cm³). After the solution was refluxed for 30 min, a solution of L (0.7 mmol) in ethanol (8 cm³) was added at room temperature, and this reacted rapidly to yield a cream precipitate. The reaction mixture was stirred for 2 h and the solid was collected by filtration, washed with cold ethanol (5 cm³) and diethyl ether (3 × 5 cm³), and dried in vacuo over P_4O_{10}. Recrystallization of the complexes can be affected from methanol. Yields were in the 60–70% range.

Colours, analytical results and molar con-

ductivity values for the prepared complexes are given in Table 1.

X-ray crystallographic studies

Suitable single crystals of $[ZnCl_2L] \cdot 0.5MeOH$ were grown by vapour diffusion of Et_2O into a solution of microcrystalline product in anhydrous MeOH at room temperature. Crystals of $[Hg_2Br_4L_2]$ were obtained by slow cooling of a hot concentrated solution of this complex in MeOH. Crystal data and details of the data collection and data processing are listed in Table 2. Data for $[ZnCl_2L] \cdot 0.5MeOH$ and $[Hg_2Br_4L_2]$ were collected on Siemens $P2_1$ and Siemens P4-RA automated diffractometers, respectively. The unit cell parameters were determined by least-squares fit of 15 centred reflections. Throughout the data collection, three reflections were monitored periodically and no decay was observed.
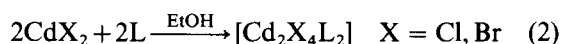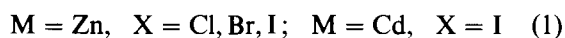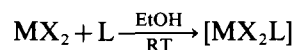
Both structures were solved by standard heavy atom/difference Fourier techniques. The computations were carried out using two versions of SHELX.[20] In the zinc(II) structure, atoms C(14) (lying on a centre of symmetry), O(15) and O(16) (see supplementary material) comprise a pair of disordered methanol solvate molecules per unit cell, with occupancy factors of 0.50, 0.25 and 0.25, respectively. For the zinc(II) compound, all non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. All the ligand's hydrogen atoms were placed in fixed, calculated positions and included in the latter refinement cycles; no hydrogen atoms were placed on the disordered solvate molecule. For the mercury(II) complex, the non-hydrogen atoms were readily located, but only the mercury and bromine atoms were refined with anisotropic thermal parameters,

the carbon and nitrogen atoms being refined isotropically. No attempt to find or include hydrogen atoms was made.

RESULTS AND DISCUSSION

Preparation and properties of the complexes

2-(2'-Pyridyl)quinoxaline (L) reacted with the zinc(II) and cadmium(II) halides in molar ratios of 0.5:1 and 1:1. Compounds of 1:1 stoichiometry were isolated in both cases; the preparation of the complexes is summarized in eqs (1) and (2):

$$MX_2 + L \xrightarrow{\frac{EtOH}{RT}} [MX_2L]$$

$$M = Zn, \quad X = Cl, Br, I; \quad M = Cd, \quad X = I \quad (1)$$

$$2CdX_2 + 2L \xrightarrow{EtOH} [Cd_2X_4L_2] \quad X = Cl, Br \quad (2)$$

A point of synthetic interest is the fact that the amount of H_2O in the starting materials and solvents affects the purity of the products. Using $CdCl_2 \cdot 2H_2O$ as starting material, pure $[Cd_2Cl_4L_2]$ could be isolated only in water-free (use of triethyl ortho-formate, reflux) reaction mixtures.

The complexes are microcrystalline, stable in atmospheric conditions and soluble in $CHCl_3$, warm MeOH, $MeNO_2$, DMF and DMSO, but to varying extents; the chloro and bromo compounds of cadmium(II) are less soluble in $CHCl_3$ and $MeNO_2$. The Λ_M values in DMSO are in accord with the six complexes being formulated as practically non-electrolytes.[21] X-ray powder diffraction patterns in the $4° < 2\theta < 60°$ range indicate that each solid represents a definite compound, which is not contaminated with starting materials. The data

Table 1. Analytical results $(\%)^a$, colours and conductivity data of the complexes of zinc(II) and cadmium(II) with L

Complex	M	X	C	H	N	Colour	$\Lambda_M{}^d$ (S cm^2 mol^{-1})
$[ZnCl_2L]^b$	18.9 (19.0)	20.6 (20.6)	45.7 (45.5)	2.6 (2.6)	12.1 (12.2)	beige	3
$[ZnBr_2L]$	14.9 (15.1)	37.1 (37.0)	36.3 (36.1)	2.0 (2.1)	9.5 (9.7)	cream	4
$[ZnI_2L]$	12.6 (12.4)	47.8 (48.2)	30.0 (29.7)	1.7 (1.7)	7.9 (8.0)	yellow	2
$[Cd_2Cl_4L_2]$	29.3 (28.8)	18.3 (18.1)	39.7 (40.0)	2.4 (2.3)	10.7 (10.8)	cream	7
$[Cd_2Br_4L_2]$	23.6 (23.4)	32.9 (33.3)	c	c	c	beige	9
$[CdI_2L]$	19.4 (19.6)	44.7 (44.3)	26.9 (27.2)	1.8 (1.6)	7.3 (7.3)	pale yellow	5

^{a} Calculated values in parentheses.

^{b} The crystallographic studies (see text) confirmed the formulation $[ZnCl_2L] \cdot 0.5MeOH$, but dried powders analysed for $[ZnCl_2L]$, suggesting MeOH loss; this was supported by the non-appearance of MeOH peaks in the IR spectrum of the dried powder.

^{c} No data available.

^{d} Values of molar conductivity for ca 10^{-3} M solutions in DMSO at 25°C.

Table 2. Crystallographic data for complexes $[ZnCl_2L]$ and $[Hg_2Br_4L_2]$

| Parameter	$[ZnCl_2L]\cdot 0.5$ MeOH	$[Hg_2Br_4L_2]$
Formula	$C_{13.5}H_{11}N_3O_{0.5}Cl_2Zn$	$C_{26}H_{18}N_6Br_4Hg_2$
M_r (g mol^{-1})	359.55	1135.28
Crystal colour and habit	Colourless prisms	Colourless needles
Crystal size (mm)	$0.50 \times 0.30 \times 0.20$	$0.06 \times 0.16 \times 0.40$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	7.426(1)	7.484 (2)
b (Å)	12.671(3)	15.947(2)
c (Å)	15.373(3)	11.442(2)
β (°)	94.49(3)	91.56(2)
V (Å^3)	1442.1(5)	1365.0(5)
Z	4	2
D_{calc} (g cm^{-3})	1.650	2.718
μ (mm^{-1})	2.070	26.986
$F(000)$	716	1032
Radiation (λ, Å)	Mo-K_α(0.71073)	Cu-K_α(1.54178)
Temperature	298	298
2θ range (°)	2.1–22.5	2.0–102.0
Scan speed (° min^{-1})	Variable (5.00–29.00 in ω)	Variable (5.00–60.00 in ω)
Scan range (°)	1.20	0.80
Range h	-1 to 7	-7 to 7
Range k	-1 to 13	0 to 15
Range l	-16 to 16	0 to 11
Reflections collected	2607	1368
Reflections unique	1858 ($R_{int} = 2.57\%$)	1368 ($R_{int} = 0.00\%$)
Reflections used $[F > n\sigma F]$	1590 ($n = 4.0$)	1196 ($n = 4.0$)
Absorption correction	DIFABS	DIFABS
Quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
Weighting scheme	Unit weights	Unit weights
Parameters refined	197	92
Largest and mean Δ/σ	0.121, 0.072	0.245, 0.037
Data-to-parameter ratio	8.1 : 1	13.0 : 1
R (%)	3.78	4.93
R_w (%)	3.90	5.91

indicate that the complexes $[ZnCl_2L]$ (unsolvated form; see footnote b in Table 1), $[ZnBr_2L]$ and $[ZnI_2L]$ are nearly isostructural; the pattern of $[CdI_2L]$ resembles very much that of $[ZnI_2L]$. The patterns of $[Cd_2Cl_4L_2]$ and $[Cd_2Br_4L_2]$ show that these complexes are isostructural with the corresponding Hg^{II} compounds, whose centrosymmetric dinuclear structures have been established by crystallography (ref. 15 and see below). We had hoped to structurally characterize one of the cadmium(II) complexes by single-crystal X-ray crystallography, but were thwarted on numerous occasions by twinning problems; thus, their characterization was based on spectroscopic studies.

The thermal decomposition of the complexes was studied using TG/DTG/DTA techniques under nitrogen. The data for the zinc(II) complexes pre-sent no special interest; their decomposition is characterized by rather simple degradation mechanisms as revealed by the small number of DTG (three) and DTA (three; two endothermic and one exothermic) peaks. These complexes decompose without the formation of thermally stable intermediates; also, no stoichiometric compounds could be assigned to the curves' inflections. The final decomposition products of the three complexes sublime partially above ca 550°C. The thermal stability sequence—as indicated by the temperature of initial mass loss—is: chloro complex (274°C) < bromo complex (296°C) < iodo complex (310°C).

The complex $[Cd_2Cl_4L_2]$ decomposes via stoichiometric, stable intermediates. The TG/DTG curves showed an initial, endothermic weight loss between 202 and 265°C, which corresponded to the release of one L molecule (found : 25.8 ; calc. :

26.5%). A plateau is reached at 268 up to 300°C. The thermally stable pale yellow product, obtained after a TG experiment up to 275°C, was isolated and studied using the same physical and spectroscopic methods as those used in this work; the results of this study will be presented below. There are two other very distinct TG inflections in the ranges 300–365 (one endothermic DTA peak) and 470–590°C (one endothermic DTA peak followed by a sharp exothermic one). The weight loss in the first of these inflections corresponded very well to the formation of two moles of $CdCl_2$ per mole of $[Cd_2Cl_4L_2]$ (found: 26.1; calc.: 26.5%). The last decomposition step at 470–590°C may consist of a combination of sublimation and transformation of $CdCl_2$ into CdO, as indicated by the low percentage of the residue (15.3%) and the appearance of two DTA peaks. It is a matter of interest that the species with the empirical formula Cd_2Cl_4L has been isolated in pure form from a solid-state reaction [eq. (3)], whilst attempts for its preparation from solution have been unsuccessful.

$$n[Cd_2Cl_4L_2] \xrightarrow[N_2]{202-265°C} [Cd_2Cl_4L]_n + nL \quad (3)$$
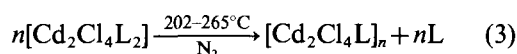
Compound $[Cd_2Br_4L_2]$ loses the two L molecules in the 251–340°C range in one single endothermic step (found: 42.6; calc.: 43.3%). Cadmium(II) bromide sublimes between 420 and 550°C, leaving a residue of 2.5% above 555°C. The iodo complex starts to decompose at 255°C. The decomposition is very complex, as revealed by the appearance of five DTG maxima and six DTA peaks. No stable intermediates were observed; repeated thermograms for this complex showed low and varying final decomposition patterns, indicating partial sublimation.

Description of structures

The structures of complexes $[ZnCl_2L] \cdot 0.5MeOH$ and $[Hg_2Br_4L_2]$ are shown in Figs 1 and 2, respectively. Selected metric parameters are presented in Tables 3 and 4.*

The unit cell of the zinc(II) complex contains four molecules of $[ZnCl_2L]$ and two MeOH molecules of crystallization. The zinc(II) atom is tetrahedrally surrounded by the two halogens and the nitrogen
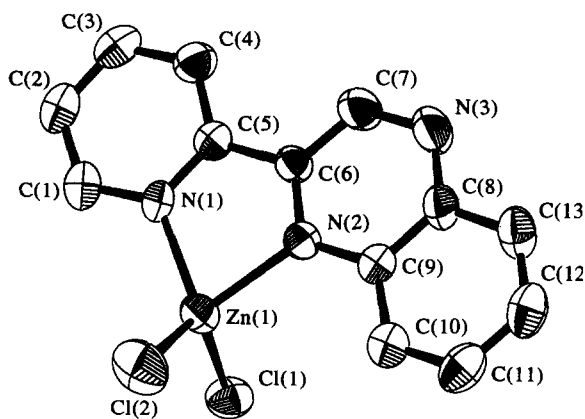

Fig. 1. Molecular structure of $[ZnCl_2] \cdot 0.5MeOH$ with the atom labelling scheme. The methanol molecule is not shown.
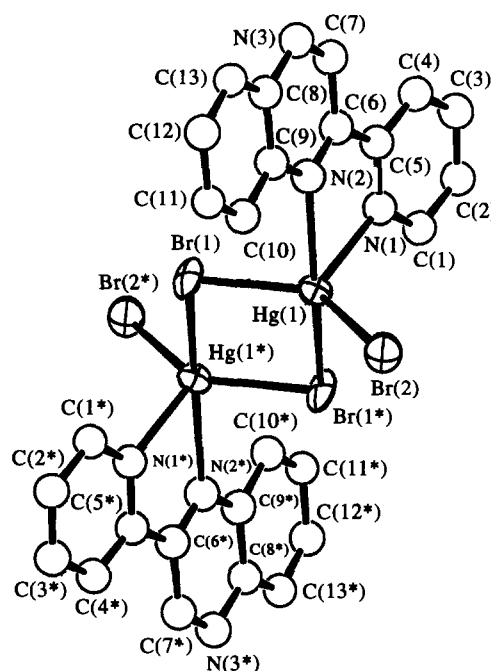

Fig. 2. Molecular structure of $[Hg_2Br_4L_2]$. Asterisks are used for symmetry-related atoms.

atoms N(1) and N(2); L acts as a bidentate chelating ligand, giving a five-membered ring. In contrast to the conformation of free L,[15] in the coordinated L molecule the pyridine nitrogen and the nearest quinoxaline nitrogen are located on the same side of the carbon–carbon bond which connects the two rings; this is a consequence of the chelating effect. The angle between the best planes of the pyridine and quinoxaline rings is 3.7(1)°. The Zn—Cl distances of 2.188(2) and 2.213(2) Å are in the expected range for metal complexes with ZnN_2Cl_2 distorted tetrahedral environments.[17,22–26] The Zn—N bond lengths are normal for this class

---

*Supplementary material available. Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles and calculated and observed structure factors for both complexes have been deposited.

Table 3. Selected bond distances (Å) and angles (°) for [ZnCl$_2$L] · 0.5MeOH

Zn(1)—Cl(1)	2.213(2)	C(1)—N(1)	1.337(6)
Zn(1)—Cl(2)	2.188(2)	C(5)—N(1)	1.333(6)
Zn(1)—N(1)	2.058(4)	C(6)—N(2)	1.310(6)
Zn(1)—N(2)	2.084(4)	C(9)—N(2)	1.373(6)
Cl(1)—Zn(1)—Cl(2)	118.5(1)	N(1)—Zn(1)—N(2)	79.8(1)
Cl(1)—Zn(1)—N(1)	110.9(1)	Zn(1)—N(1)—C(1)	126.2(3)
Cl(1)—Zn(1)—N(2)	107.3(1)	Zn(1)—N(1)—C(5)	114.4(3)
Cl(2)—Zn(1)—N(1)	117.8(1)	Zn(1)—N(2)—C(6)	112.9(3)
Cl(2)—Zn(1)—N(2)	116.0(1)	Zn(1)—N(2)—C(9)	128.1(3)

Table 4. Selected bond distances (Å) and angles (°) for [Hg$_2$Br$_4$L$_2$]^a

Hg(1)—Br(1)	2.588(2)	C(1)—N(1)	1.352(25)
Hg(1)—Br(1*)	2.917(2)	C(5)—N(1)	1.353(25)
Hg(1)—Br(2)	2.524(2)	C(6)—N(2)	1.283(25)
Hg(1)—N(1)	2.366(16)	C(9)—N(2)	1.386(25)
Hg)1)—N(2)	2.489(16)	Hg(1)...Hg(1*)	4.060(2)
Br(1)—Hg(1)—Br(1*)	85.2(1)	Br(2)—Hg(1)—N(2)	99.3(4)
Br(1)—Hg(1)—Br(2)	137.2(1)	N(1)—Hg(1)—N(2)	68.1(5)
Br(1)—Hg(1)—N(1)	109.7(4)	Hg(1)—N(1)—C(1)	119.1(13)
Br(1)—Hg(1)—N(2)	88.4(4)	Hg(1)—N(1)—C(5)	118.5(13)
Br(1*)—Hg(1)—Br(2)	99.9(1)	Hg(1)—N(2)—C(6)	115.5(12)
Br(1*)—Hg(1)—N(1)	94.2(4)	Hg(1)—N(2)—C(9)	124.4(12)
Br(1*)—Hg(1)—N(2)	157.8(4)	Hg(1)—Br(1)—Hg(1*)	94.8(1)
Br(2)—Hg(1)—N(1)	112.3(4)		

^{a}Asterisks are used for the symmetry-related atoms.

of compounds.[22-25,27,28] Deviation from regular tetrahedral geometry is indicated by the large Cl(1)—Zn(1)—Cl(2) (118.5(1)°], Cl(2)—Zn(1)—N(1) [117.8(1)°] and Cl(2)—Zn(1)—N(2) [116.0(1)°] angles and the correspondingly small N(1)—Zn(1)—N(2) [79.8(1)°] angle. The preferred small bite angle of the bidentate L and interligand repulsion between the chlorides presumably are responsible for the observed distortion.[23,25]

The structure of [Hg$_2$Br$_4$L$_2$] consists of dinuclear molecules with two bridging bromo ligands; a terminal bromo ligand and a chelating L molecule complete five-coordination at each mercury(II) atom. The bridging Hg$_2$Br$_2$ unit is constrained to be planar by the presence of the crystallographic inversion centre in the middle of the dimer. The mercury–bridging bromo distances [2.588(2), 2.197(2) Å] are longer than the mercury–terminal bromo distance [2.524(2) Å, as expected. The bridging bonds in the present compound are nevertheless shorter than the long bridging contacts found in the structures of other bromo mercury(II) complexes with effective coordination number five.[29-31] The

Hg—N bond lengths are normal for this kind of compound and indicate bonds of intermediate strength.[18,29-32] There is a difference (ca 0.12 Å) in bond length between the two Hg—N bonds (the corresponding difference in [ZnCl$_2$L] · 0.5MeOH is ca 0.02 Å), with the metal to pyridine-nitrogen [N(1)] distance being shorter in both cases. The different metal–nitrogen bond lengths may reflect a difference in donor strength of the respective nitrogen atoms. In [Cu$_2$Cl$_4$L$_2$],[13,14] however, the copper to pyridine-nitrogen distance [2.106(5) Å] is longer than the copper to quinoxaline-nitrogen distance [2.021(5) Å], emphasizing the importance of the metal ion in determining the relative donor strength of the two nitrogen atoms.

The coordination geometry about mercury(II) is distorted trigonal bipyramidal. The apical sites are occupied by Br(1*) and N(2), with atoms Br(1), Br(2) and N(1) making up the equatorial plane. The mercury(II) atom is displaced out of the equatorial plane by 0.130 Å in the direction of Br (1*). On the basis of bond strength,[32,33] the distorted trigonal bipyramidal geometry can be described in terms

of a $(3+2)$ coordination with three donor atoms strongly bonded in the equatorial plane and two weaker bonds in axial positions. The two individually planar portions of L in $[Hg_2Br_4L_2]$ (the pyridine and the quinoxaline ring) are slightly twisted out of coplanarity, the dihedral angle between the two planes being $7.0°$. In the free ligand,[15] the two planar moieties are more coplanar, the planes making an angle of $3.4°$.

The closest precedent of $[Hg_2Br_4L_2]$ is centrosymmetric $[Hg_2Br_4(bpy)_2]$ (bpy = 2,2-bipyridine), but the authors[31] prefer to describe its geometry as square pyramidal with the terminal bromine at the apex; however, in the extensive collection of structural information on mercury(II) halide complexes by Dean,[29] the coordination polyhedron of this compound has been described as distorted trigonal bipyramidal. The structure of $[Hg_2Br_4L_2]$, as detailed in the discussion above and in Table 4, shows remarkable similarity to that of $[Hg_2Cl_4L_2]$.[15] Obviously, the replacement of Cl^- by Br^- has little structural effect.

IR and Raman spectra

The IR spectrum of the crystals of $[ZnCl_2L]\cdot0.5MeOH$ shows a weak, broad band at *ca* 3470 cm^{-1} due to the O—H stretching vibration of lattice MeOH.

The mid-IR and Raman spectra of the zinc(II) and cadmium(II) complexes are similar to those of other metal complexes with L.[12-15] The characteristic IR in-plane and out-of-plane pyridine-ring bands at 620 and 401 cm^{-1}, respectively, are shifted upwards in the complexes (including the product Cd_2Cl_4L), showing the involvement of the pyridine nitrogen N(1) in coordination.[34] The *ca* 950 cm^{-1} region is viewed as the key to differentiating between monodentate and bidentate bridging coordination of the quinoxaline ring.[35,36] The spectrum of the free ligand shows a strong band at 960 cm^{-1}. The appearance of a single, sharp band at 965–975 cm^{-1} in the spectra of the 1 : 1 complexes, i.e. the fact that this band does not split on complexation, characterizes a monodentate quinoxaline coordination,[36] in agreement with the results of the crystal structure determinations. This vibration also appears in the Raman spectra of the complexes at the same frequency. This spectral region is distinctly different in the 2 : 1 complex with the empirical formula Cd_2Cl_4L, which was prepared by solid-state thermal decomposition of $[Cd_2Cl_4L_2]$; the splitting of the strong L band at 960 cm^{-1} into a triplet in the spectrum of Cd_2Cl_4L is indicative of participation of both quinoxaline nitrogens N(2) and N(3) in coordination.[3-5]

The low-frequency region $(400$–100 cm$^{-1})$ of L has few weak IR and Raman bands. This would indicate that some of the other bands observed in this region in the spectra of the complexes would be assignable to metal–donor atom vibrations. Assignments of far-IR and Raman metal–ligand stretching vibrations in Table 5 have been carefully given by studying : (1) the frequencies of the internal modes of L; (2) bands principally dependent on X (X = Cl, Br, I) for a given metal; (3) the variation in band frequency with changing metal (zinc(II), cadmium(II)) for a given X; and (4) extensive literature reports.[12,15,17,24,34,37-39]

In $[ZnCl_2L]$, the metal ion is involved in a distorted tetrahedral N_2ZnCl_2 skeleton. Assuming a virtual C_{2v} symmetry for this complex, both the antisymmetric and symmetric $ZnCl_2$ and ZnN_2 stretching vibrations are IR and Raman-active. Complexes $[ZnX_2L]$ (X = Cl, Br, I) and $[CdI_2L]$ present two well-resolved far-IR bands attributable to metal–halogen stretching vibrations and two bands due to $v(M—N)$. For $[ZnBr_2L]$ and $[CdI_2L]$ the corresponding Raman spectra show only one strong $v(M—N)$ band, which is assigned to the symmetric MN_2 vibration, as this mode is expected to present a higher Raman intensity than the antisymmetric one. The observed wavenumbers of the $v(M—N)_t$ modes perfectly agree with the literature data for other monomeric tetrahedral dihalogen zinc(II) and cadmium(II) complexes.[17,24,34,37,38] Thus, the described spectroscopic behaviour is consistent with the X-ray structure of the zinc(II) chloro complex and suggests the same molecular structure for $[ZnX_2L]$ (X = Br, I) and $[CdI_2L]$. For the zinc(II) complexes, the $v(Zn—N)$ vibrations shift to higher frequencies according to the sequence chloro complex < bromo complex < iodo complex, implying stronger Zn—N bonds in the same sequence. This trend is in accord with the thermal data, which show that the thermal stability of the complexes also follows the same sequence; assuming that decomposition starts with disruption of the Zn—N bonds, stronger Zn—N bonds result in thermally more stable complexes.

The IR and Raman spectra of $[Cd_2X_4L_2]$ (X = Cl, Br) and the 2 : 1 product Cd_2Cl_4L show one clear terminal Cd—X stretching and two bands in the bridging stretch region. Thus, the spectra seem incompatible with a monomeric skeleton, but they can be explained on the basis of dimeric or polymeric halide-bridged structures, while the complexes still contain terminal Cd—X bonds. It should be recalled at this point that, according to X-ray powder patterns, compounds $[Cd_2Cl_4L_2]$ and $[Cd_2Br_4L_2]$ are isostructural with $[Hg_2Cl_4L_2]$ and $[Hg_2Br_4L_2]$, respectively; the centrosymmetric, dou-

Table 5. IR[a] and Raman metal–ligand vibrational stretching frequencies (cm^{-1}) for the zinc(II) and cadmium(II) complexes of L

Complex	Technique	$v(M—X)_t$	$v(M—X)_b$	$v(M—N)$
[ZnCl$_2$L]	IR	337s,[b] 306m		216m, 202 m
	R	329m,[b] 313s		213m, 207s
[ZnBr$_2$L]	IR	259s, 237s		220sh, 207m
	R	255w, 237s		222s
[ZnI$_2$L]	IR	215s,[c] 184m		233m, 215s[c]
	R	211w, 182s		229w, 207m
[Cd$_2$Cl$_4$L$_2$]	IR	297mb	233mb, 190m[b]	183m, 175m
	R	293m	228m, 190m[b]	177s
Cd$_2$Cl$_4$L[d, e]	IR	276m	238m, 197sb[c]	197sb,[c] 183m, 175w
[Cd$_2$Br$_4$L$_2$]	IR	215m	172m,[c] 159m	193s,[b] 172 m[c]
	R	208m	174s, 155w	194m,[b] 181w
[CdI$_2$]	IR	168s, 163s		200s, 175sh
	R	168w, 158s		190s

[a] Fourier transform spectra.
[b] Overlapping with a vibration of L.
[c] Coincident bands.
[d] This product has been prepared by the thermal decomposition of [Cd$_2$Cl$_4$L$_2$] (see text).
[e] No satisfactory Raman spectra could be obtained.
Abbreviations: b = broad, m = medium, M = metal, $v(M—X)_t$ = the stretching vibration of the terminal M—X bond, $v(M—X)_t$ = the stretching vibrations of the M—X bonds in the bridging MX$_2$M groups, s = strong, sh = shoulder, X=Cl, Br, I.

bly halide-bridged, dinuclear structures of the latter have been established by X-ray crystallography. The $v(Cd—N)$ wavenumbers are higher in the iodo complex than in [Cd$_2$X$_4$L$_2$] (X = Cl, Br), probably due to the lower coordination number in [CdI$_2$L].

^{1}H NMR spectroscopy

The ^{1}H NMR spectra of the six 1 : 1 complexes in DMSO-d_6 are very similar to one another; data for two representative complexes are given in Table 6. The ^{1}H NMR assignments were based on comparisons with data for L,[12] its mercury(II) complexes[15] and a number of diamagnetic metal complexes with related ligands.[7,40] The two-dimensional COSY NMR spectra of [ZnCl$_2$L] and [Cd$_2$Cl$_4$L$_2$] were also obtained, to further confirm the assignments of the observed resonances. For example, on the basis of the assignment[12] of 9.06 ppm to H(1) in [ZnCl$_2$L], the cross-peak to this resonance leads to the assignment of H(2) at 7.75 ppm. The cross-peak at the chemical shift coordinates 7.75 and 8.19 ppm identifies the H(3) proton at 8.19 ppm and so on. The spectrum of the 2 : 1 compound Cd$_2$Cl$_4$L could not be recorded because of its low solubility in DMSO (the insolubility of this compound in a variety of organic solvents is an indication that it has a polymeric structure).

The electron density on the pyridine ring of L

diminishes upon coordination to metal ions, inducing a downfield shift of H(1) (ca 9.10 ppm in the complexes vs 8.94 ppm in free L).[40,41] The downfield shift observed for H(7) is insignificant (< 0.03 ppm), suggesting that the N(3) atom of the quinoxaline ring remains non-coordinated in the complexes; a downfield shift would be expected if coordination had occurred.

CONCLUSIONS

According to spectroscopic studies and X-ray analysis, we classify the zinc(II), cadmium(II) and mercury(II) complexes of L into three classes. Results are reported in Table 7. Class A contains monomeric, distorted tetrahedral complexes and class B dinuclear, doubly halogen-bridged, five-coordinated complexes. In both classes A and B, L acts as a chelating N(1), N(2) ligand. The only member of class C is the product of reaction (3). IR evidence suggests a bridging mixed bidentate chelating N(1), N(2)-monodentate N(3) ligation mode for L in this product; a complex polymeric structure with tridentate bridging L molecules and both terminal and bridging chlorides, is tentatively proposed for Cd$_2$Cl$_4$L. It seems that the ratio between the metal and the halogen radii decides the coordination geometry. When the halogen size is increased and/or the metal size is decreased, the

Table 6. 200 MHz ^{1}H NMR spectral data[a, b] of the representative complexes [ZnCl$_2$L] and [Cd$_2$Cl$_4$L$_2$] in DMSO-d_6

	[ZnCl$_2$L]		[Cd$_2$Cl$_4$L$_2$]	
Proton	δ (ppm)	J_{H-H}(Hz)[c]	δ (ppm)	J_{H-H}(Hz)[c]
H(1)	9.07mt	1,2 = 4.78	9.05mt	1,2 = 4.74
H(2)	7.75mt	1,3 = 1.10	7.77mt	1,3 = 0.78
H(3)	8.19mt	1,4 = 0.69	8.20mt	1,4 = 0.78
H(4)	8.70mt	2,3 = 5.08	8.71mt	2,3 = 6.10
H(7)	10.00s	2,4 = 1.74	10.02s	2,4 = 1.48
H(10)	8.36mt	3,4 = 7.94	8.40mt	3,4 = 7.75
H(11)	8.05mt		8.06mt	
H(12)	7.99mt		7.99mt	
H(13)	8.27mt		8.26mt	

[a] Spectra recorded at ambient temperature.

[b] The spectra were run ca 10 min after dissolution.

[c] Due to complex nature of the four-spin system of protons H(10)–H(13), direct calculation of their coupling constants is not possible.

Abbreviations: mt = multiplet, s = singlet.

Table 7. Structural types[a] of zinc(II), cadmium(II) and mercury(II) halide complexes of L

	X		
M	Cl	Br	I
Zn[b]	A	A	A
Cd[b]	B	B	A
Cd[c]	C	[d]	[d]
Hg[b,e]	B	B	A

[a] For a detailed discussion, see text (Conclusions).

[b] Complexes with an 1 : 1 stoichiometry.

[c] Complex with a 2 : 1 stoichiometry, i.e./Cd$_2$Cl$_4$L; this compound has been prepared by the solid-state reaction shown in eq. (3).

[d] No product avaialble.

[e] Reference 15 and this work.

tetrahedral coordination is preferred because of the difficulty of accommodating three rather than two large halogen atoms around a small metal centre.

The spectroscopic evidence for the tridentate bridging behaviour of L in the 2:1 compound Cd$_2$Cl$_4$L now encourages us to move on to the logical next phase of this work, the attempted preparation, crystallization and structural characterization of metal complexes with mixed bidentate–monodentate L molecules. As zinc(II), cadmium(II) and mercury(II) do not give complexes from solution with such behaviour of L (even in low L : metal ratios), future work will be and is being performed with other metal ions. More recent

work has also unearthed a novel mercury(II) complex, in which L acts as a monodentate ligand; this unexpected result will be described in due course. Work is also in progress for the preparation and characterization of heterobimetallic complexes of L with selective coordination of metals at the different coordination sites.

REFERENCES

1. J. Reedijk, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 2, Ch. 13.2, p. 73. Pergamon Press, Oxford (1987).
2. E. C. Constable, *Adv. Inorg. Chem.* 1989, **34**, 1.
3. E. C. Constable and P. J. Steel, *Coord. Chem. Rev.* 1989, **93**, 205.
4. Md. A. Masood and D. J. Hodgson, *Inorg. Chem.* 1993, **32**, 4839 and refs therein.
5. J. P. Sauvage, *Accts Chem. Res.* 1990, **23**, 319.
6. J. C. Chambron, D. K. Mitchell and J. P. Sauvage, *J. Am. Chem. Soc.* 1992, **114**, 4625.
7. S. Campagna, G. Denti, G. De Rosa, L. Sabatino,

M. Ciano and V. Balzani, *Inorg. Chem.* 1989, **28**, 2565.

8. K. Bierig, R. J. Morgan, S. Tysoe, H. D. Gafney and T. C. Strekas, *Inorg. Chem.* 1991, **30**, 4898.

9. V. P. Mamaev, O. P. Shkurko and S. G. Baram, *Adv. Heterocyclic Chem.* 1987, **42**, 1.

10. P. J. Steel, *Coord. Chem. Rev.* 1990, **106**, 227.

11. W. Kaim, *Angew. Chem., Int. Edn Engl.* 1983, **22**, 171.

12. S. Kasselouri, A. Garoufis, A. Katehanakis, G. Kalkanis, S. P. Perlepes and N. Hadjiliadis, *Inorg. Chim. Acta* 1993, **207**, 255.

13. J. C. Plakatouras, N. Hadjiliadis, S. P. Perlepes, A. Albinati and G. Kalkanis, *Polyhedron* 1993, **12**, 2069.

14. E. G. Bakalbassis, J. Mrozinski, S. P. Perlepes, N. Hadjiliadis, F. Lianza and A. Albinati, *Polyhedron* 1994, **13**, 3209.

15. S. Kasselouri, A. Garoufis, S. Paschalidou, S. P. Perlepes, I. S. Butler and N. Hadjiliadis, *Inorg. Chim. Acta* 1994, **227**, 129.

16. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, pp. 1395–1422. Pergamon Press, Oxford (1984).

17. F. Cariati, G. Ciani, L. Menabue, G. C. Pellacani, G. Rassu and A. Sironi, *Inorg. Chem.* 1983, **22**, 1897.

18. M. Louloudi, N. Hadjiliadis, J.-A. Feng, S. Sukumar and R. Bau, *J. Am. Chem. Soc.* 1990, **112**, 7233.

19. J. C. Plakatouras, S. P. Perlepes, D. Mentzafos, A. Terzis, T. Bakas and V. Papaefthymiou, *Polyhedron* 1992, **11**, 2657.

20. (a) G. M. Sheldrick, SHELX 76, University of Cambridge, U.K. (1976); (b) G. M. Sheldrick, SHELX 86, University of Gottingen, Germany (1986).

21. W. J. Geary, *Coord. Chem. Rev.* 1971, **7**, 81.

22. C. W. Reimann, S. Block and A. Perloff, *Inorg. Chem.* 1966, **5**, 1185.

23. H. S. Preston and C. H. L. Kennard, *J. Chem. Soc.* (*A*) 1969, 1956.

24. W. L. Steffen and G. J. Palenik, *Inorg. Chem.* 1977, **16**, 1119.

25. W. B. Tolman, S. Liu, J. G. Bentsen and S. J. Lippard, *J. Am. Chem. Soc.* 1991, **113**, 152.

26. J. M. Salas, M. A. Romero and A. Rahmani, *Acta Cryst.* 1994, **C50**, 510.

27. P. D. Verweij, F. J. Rietmeijer, R. A. G. De Graaff, A. Erdonmez and J. Reedijk, *Inorg. Chim. Acta* 1989, **163**, 223.

28. J. Lipkowski, *J. Coord. Chem.* 1990, **22**, 153.

29. P. A. W. Dean, *Prog. Inorg. Chem.* 1978, **24**, 109.

30. W. Levason and C. A. McAuliffe, in *The Chemistry of Mercury* (Edited by C. A. McAuliffe), pp. 60–135. MacMillan, London (1977).

31. D. C. Craig, Y. Farhangi, D. P. Graddon and N. C. Stephenson, *Cryst. Struct. Commun.* 1973, **3**, 155.

32. M. Authier-Martin and A. L. Beauchamp, *Can. J. Chem.* 1977, **55**, 1213.

33. P. Biscarini, L. Fusina, G. Nivellini and G. Pelizzi, *J. Chem. Soc., Dalton Trans.* 1981, 1024.

34. R. J. H. Clark and C. S. Williams, *Inorg. Chem.* 1965, **4**, 350.

35. P. Lumme, S. Lindroos and E. Lindell, *Acta Cryst.* 1987, **C43**, 2053.

36. P. Lumme, S. Lindroos and E. Lindell, *Inorg. Chim. Acta* 1988, **144**, 75.

37. D. A. Thornton, *Coord. Chem. Rev.* 1990, **104**, 251.

38. M. Goldstein and R. J. Hughes, *Inorg. Chim. Acta* 1980, **40**, 229 and refs therein.

39. S. P. Perlepes, D. Nicholls and M. R. Harrison, *Inorg. Chim. Acta* 1985, **102**, 61 and refs therein.

40. H. A. Nieuwenhuis, J. G. Haasnoot, R. Hage, J. Reedijk, T. L. Snoeck, D. J. Stufkens and J. G. Vos, *Inorg. Chem.* 1991, **30**, 48.

41. Th. F. Zafiropoulos, J. C. Plakatouras and S. P. Perlepes, *Polyhedron* 1991, **10**, 2405 and refs therein.