Structural Aspects of Cadmium(II) Complexes - Isomers

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ABSTRACT

The coordination chemistry of cadmium(II) covers wide fields, as shown by a survey covering the crystallographic and structural data of over 600 examples. About 8 % of those complexes exist as isomers and are summarised. Included are distortion (91.5 %), ligand isomerism (6.5 %), mixed isomerism (distortion and *cis – trans*) (1 %) and polymerisation isomerism (1 %). These are discussed in terms of the coordination about the cadmium atom, and correlations are drawn between donor atom, bond lengths and interbond angles. Distortion isomers, differing only by degree of distortion in Cd – L and L – Cd – L angles, are the most common.

There are four – (tetrahedrally), five – (trigonal bipyramidally), six – (pseudo octahedrally), seven – (pentagonal bipyramidally) and eight - (dodecahedrally, hexagonal bipyramidally) coordinate cadmium(II) atoms. Most common are pseudo octahedral.

Noticeably, in the chemistry of zinc(II) only two types of isomerism were formed, namely distortion (96 %) and ligand isomerism (4 %).

Keywords: cadmium(II) complexes, structure, isomers

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0. ABBREVIATIONS

acac	acetylacetonate
ba	benzylamine
2,2'-bpy	2,2'-bipyridine
bsn	1,3-bis(methylamino)-2,2'- dimethylpropane
$C_6H_5O_3$	3-hydroxy-2-methyl-4-pyrone(-)
$C_7H_4NS_2$	benzothiazole-2-thiolate
$C_7H_8O_2$	2,6-dimethyl-4H-pyran-4-one
dmpd	2,3-dimethylpropane-1,3-diamine
dmpzea	2-(3,5-dimethyl-1-pyrazolyl)ethyl)oxide
dmso	dimethylsulphoxide
en	ethylenediamine
Et	ethyl
Et_2dtc	diethyldithiocarbamate
HB	hydroborane
hxg	hexagonal
L_{ap}	apical ligand
L_{eq}	equatorial ligand
m	monoclinic
mal	maleate
Me	methyl
Me_4en	N,N,N',N'-tetramethylethylenediamine
2-Mepy	2-methylpyridine
3-Mepy	3-methylpyridine
4-Mepy	4-methylpyridine
$4\text{-}MeC_6H_4S$	4-methylbenzenethiol
$(3,5\text{-}Me_2pz)_3$	tris(3,5-dimethylpyrazole)
mtt	*cis*-1-methylthiostilbene-2-thiolate
$4\text{-}NH_2bz$	4-aminobenzoate
or	orthorhombic
Ph	phenyl
phen	1,10-phenanthroline
$Ph_2PC_2H_4NEt_2$	1-diethylamino-2-diphenylphopsphinoethane
$Pr^i_3C_6H_2S$	2,4,6-tris(iso-propyl)benzenethiol
pt	N-oxopyridine-2-thionate
py	pyridine
tac	1,4,7-triazacyclononane
tg	tetragonal

tmtact	1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane
tr	triclinic
trg	trigonal
tsc	thiosemicarbazide

1. INTRODUCTION

The chemistry of cadmium has been an active area of research, particularly in the fields of catalysis and *biochemistry*. Unlike zinc, cadmium does not appear to play any role as an essential trace element in bio – systems; on the contrary, it is a highly toxic element to a wide variety of living organisms including man.

The importance of the relationship between structure and reactivity has been widely demonstrated. Systematic studies in the field of complex compounds over the last 50 years have become of increasing interest. Stereoselectivity in complex compounds is very often related to important stereospecificity of biological systems, catalysis and stereochemical effects in technical processes. It is well known that isomers are substances that have the same number and kinds of atoms arranged differently. Because their structures are different, isomers have different properties. Isomers can be broadly classed into two main categories, structural and stereoisomers. The former can be divided into ionisation, hydrate, coordination number, linkage and polymerisation sub – categories. The latter can be divided into geometric (*cis – trans, fac – mer*), optical, ligand and distortion isomerism.

Over six hundred cadmium coordination and organometallic compounds have been surveyed /1/, with almost fifty isomeric examples noted. In this review we analyse and classify these examples to show that stereoisomers are more common than structural isomers. Analysis of zinc(II) compounds showed /2/ that there are two types of isomerism distortion (96%) and ligand isomers (4%).

The systems discussed have been sorted by nuclearity, and then subdivided according to the coordination number of the cadmium(II) atom. Within each coordination number, the compounds are listed in order of increasing covalent radius of the principal coordinating ligand atom and increasing complexity of the coordination sphere.

2. DISTORTION ISOMERISM

The coexistence of two or more species, even within the same crystal, differing only by degree of distortion, is typical of the general class of distortion isomerism /3/.

2.1. Isomeric forms

The crystallographic and structural data for cadmium(II) distortion isomers are assembled in Table 1.

Table 1. Crystallographic and Structural Data for Cadmium (II) Complexes, Existing in Two and Three Distortion Isomeric Forms

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Cd – L [Å]	L – Cd – L [°]	Ref.
A: Monomers							
Cd(η^6-inomycin) (colourless)	or $P2_12_12_1$ 4	22.152(5) 18.688(3) 12.079(1)		CdO_6	O^b 2.33(-,7)	O,O^b 81-170	4
Cd(η^6-inomycin) (colourless)	m $P2_1$ 4	12.132(2) 33.991(14) 13.191(3)	116.0(0)	CdO_6 CdO_6	O 2.30(-,20) O 2.40(-,30)	O,O 84-177 O,O 76-162	4
B: Dodecamers							
$(NMe_4)_4[Cd_{10}(\mu_3\text{-}S)_4(\mu\text{-}SPh)_{12}(SPh)_4]$ (colourless)	tg I4 2	20.946(2) 14.779(2)		CdS_4 (x2) CdS_4 (x4) CdS_4 (x4)	μ_3S 2.485(2) μPhS 2.600(2) μ_3S 2.489(2,14) μPhS 2.620(2,8) μPhS 2.565(2,7) PhS 2.486(3)	μ_3S, μ_3S 125.0(1) μ_3S, μS 107.6(1,3) μS, μS 98.2(1) μ_3S,μ_3S 124.1(1) μ_3S,μS 106.3(1,10.7) μS, μS 104.6(1) μS, μS 106.4(1,8.3) μS, S 112.7(1,8.7)	5
$(NMe_4)_4[Cd_{10}(\mu_3\text{-}S)_4(\mu\text{-}SPh)_{12}(SPh)_4]$ (colourless)	tg I42m 2	20.140(2) 16.896(4)		CdS_4 (x2) CdS_4 (x4) CdS_4 (x4)	μ_3S 2.472(4) μPhS 2.612(6) μ_3S 2.483(7,6) μPhS 2.508(7,8) μPhS 2.566(8,18) PhS 2.459(8)	μ_3S,μ_3S 123.5(3) μ_3S,μS 107.3(2,7) μS, μS 102.1(2) μ_3S, μ_3S 125.9(3) μ_3S,μS 106.8(2,4.1) μS, μS 101.7(2) μS, μS 107.4(2,8.2) μS, S 111.5(3,1.9)	5

$(NMe_4)_4[Cd_{10}(\mu_3\text{-}S)_4(\mu\text{-}SPh)_{12}(SPh)_4]$ (colourless)	tg $P42_1c$ 2	20.007(3) 17.982(3)		CdS_4 (x2) CdS_4 (x4) CdS_4 (x4)	μ_3S 2.488 μPhS 2.596 μ_3S 2.471(-,23) μPhS 2.588(-,23) μPhS 2.551(-,7) PhS 2.447	μ_3S,μ_3S 123.2 $\mu_3S,\mu S$ 107.8(-,5.3) $\mu S,\mu S$ 100.5 μ_3S, μ_3S 125.8 $\mu_3S,\mu S$ 106.5(-,8.4) $\mu S,\mu S$ 104.0 $\mu S,\mu S$ 108.1 (-,12.9) μS,S 111.0(-,7.4)	6
C: Polymers							
$Cd(mal)(H_2O)_2$ (colourless)	m $P2_1/c$ 8	8.729(2) 14.285(6) 11.622(4)	102.66(2)	CdO_6 CdO_8	μO 2.287(4,2) H_2O 2.274(5,50) μO 2.695(5,147) O 2.199(5) – 2.782(5)	O,O 80.9-108.3(2) 164.9(2,1.1) O,O 51.6(2,1.0) 68.8-138.5(2)	7
$Cd(mal)(H_2O)_2$ (colourless)	m Cc 4	6.08(1) 16.30(1) 7.00(1)	93.8(1)	CdO_6	O 2.235(6,11) 2.423(4,98) H_2O 2.269(8,22)	O,O 54.3(2)[c] 78.8-164.3(8)	8
$(C_{10}H_{21}NH_3)_2[Cd(\mu\text{-}Cl)_2(Cl)_2]$ (colourless)	m $P2_1$ 4	7.354(1) 7.545(1) 51.620(3)	91.74(1)	$CdCl_6$			9
$(C_{10}H_{21}NH_3)_2[Cd(\mu\text{-}Cl)_2(Cl)_2]$ (colourless) (at 318 K)	or Amca 4	7.460(2) 7.549(2) 5.464(2)		$CdCl_6$			9
$(Me_3NH)[Cd(\mu\text{-}Cl)_3]$ (colourless) (at 173 K)	or Pbnm 4	8.957(2) 14.348(4) 6.6873(9)		$CdCl_6$	μCl 2.643(7,29)	μCl, μCl 84.2(1,2)	10
$(Me_3NH)[Cd(\mu\text{-}Cl)_3]$ (colourless) (at 348 K)	hxg P-6 18	26.0805(5) 6.756(11)		$CdCl_6$	μCl 2.65(1,3)	μCl, μCl not given	11
$(Me_3NH)[Cd(\mu\text{-}Cl)_3]$ (colourless) (at 355 K)	or Pbnm 8	17.123 15.256 6.731		$CdCl_6$	μCl 2.655(10,25)	μCl,μCl 90.0(1,7.6) 178.2(1,1)	12

Table 1. continued 2

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Cd – L [Å]	L – Cd – L [°]	Ref.
$(Me_3NH)[Cd(\mu\text{-}Cl)_3]$ (colourless) (at 375 K)	or Pbnm 8	17.12 15.26 6.73		$CdCl_6$	μCl 2.64(1,8)	μCl,μCl 90.0(1,8.6) 177.9(1,1.9)	13
$(Me_3NH)[Cd(\mu\text{-}Cl)_3]$ (colourless) (at 389 K)	hxg P-6 2m 6	15.105 6.763(3)		$CdCl_6$	μCl 2.65(1,4)	μCl,μCl 90.0(2,6.9) 178.8(4)	11
$(Me_3NH)[Cd(\mu\text{-}Cl)_3]$ (colourless)	hxg P-6 3m 2	9.138 6.723		$CdCl_6$	μCl 2.644(1)	μCl,μCl 90.0(1,6.1)	14
$Cd(\mu\text{-}\eta^2\text{-}NCS)_2(ba)_2$ (colourless)	m $P2_1/n$ 2	27.390(19) 5.7709(8) 5.8733(9)	90.35(3)	CdN_4S_2	μSCN 2.372(3,0) μNCS 2.754(1,0) baN 2.294(3,0)	N,N 88.1(1) N,S 89.1(1,1.4)	15
$Cd(\mu\text{-}\eta^2\text{-}NCS)_2(ba)_2$ (colourless)	m $P2_1/c$ 2	13.958(2) 5.759(1) 11.466(2)	99.24(1)	CdN_4S_2	μSCN 2.319(8,0) μNCS 2.753(2,0) baN 2.322(5,0)	N,N 86.8(2) N,S 90.0(2,8)	16
$[Cd(\mu\text{-}4\text{-}NH_2bz)_2(H_2O)]\cdot 2H_2O$ (colourless)	tr P1 2	17.798(2) 6.187(1) 8.261(2)	111.98(2) 105.0(2) 89.98(2)	CdO_5N_2	O_{eq} 2.39(1,4) H_2O_{ap}2.38(1) N_{ap} 2.43(2,2)	O,O 54,4(14,2)[c] 83.0-140.5(5) 165.3(4) O,N 90.2(5,6.1)	17
$[Cd(\mu\text{-}4\text{-}NH_2bz)_2(H_2O)]\cdot 2H_2O$ (colourless)	m C2/c 4	15.363(4) 6.195(2) 17.839(14)	108.25(4)	CdO_5N_2	O_{eq} 2.389(3,38) H_2O_{ap}2.350(4) N_{ap} 2.437(3,0)	O,O 54,74(9)[c] 75.7-139.5 165.7 O,N 170.2(1)	18

Footnotes: a) When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e. s. d. , the second is the maximum deviation from the mean.
b) The chemical identity of the coordinated atom or ligand is specified in these columns.
c) Four-member metallocyclic ring.

Colourless Cd(η^6-inomycin) /4/ exists in two isomeric forms, orthorhombic and monoclinic, and is the only example of monomeric cadmium(II) complex which exists in two isomeric forms. In addition, the monoclinic isomer contains two crystallographically independent molecules. Each Cd(II) atom has an octahedral arrangement created by a hexadentate O donor inomycin ligand (CdO_6), with a different degree of distortion. The mean Cd – O bond distance in the orthorhombic form is 2.33 Å, in the monoclinic 2.30 Å (molecule 1) and 2.40 Å (molecule 2). The O – Cd – O bond angles range from 81 to 170 ° in the orthorhombic, 84 – 177 ° in the monoclinic (molecule 1) and 76 - 160 ° (molecule 2). The degree of distortion increases in the order: monoclinic (molecule 1) < orthorhombic < monoclinic (molecule 2).

Three isomeric forms (tetragonal) are found in colourless $(NMe_4)_4[Cd_{10}(\mu_3\text{-}S)_4(\mu\text{-}SPh)_{12}(SPh)_4]$ /5,6/ and the structure of one of these is shown in Fig. 1. The ten cadmium atoms and twenty sulphur atoms are congruent with a supertetrahedral fragment of the cubic CdS lattice, and constitute four adamantanoid cages. There are six inner (Cd^i) atoms forming a tetrahedron. Four of the triangular faces are capped with (μ_3-S) ligands, and the other four are capped with (μ_3-SPh)Cd(SPh) moieties. The four outer (Cd^o) atoms describe a tetrahedron. The local coordination of the inner Cd atoms is $[Cd^i(\mu_3\text{-}S)_2(\mu\text{-}SPh)_2]$ while that of the outer atoms is $[(\mu\text{-}SPh)_3Cd^o(SPh)]$.The three isomeric forms differ by degree of distortion (Table 1) and are unique examples in cadmium chemistry. The mean Cd . . . Cd separations and Cd -μ_3S-Cd bridge angles are 3.842(1) Å and 104.7(1)° in one /5/ and 3.817(2) Å and 103.8° in the other one /5/. Such data for the third one /6/ are not available.

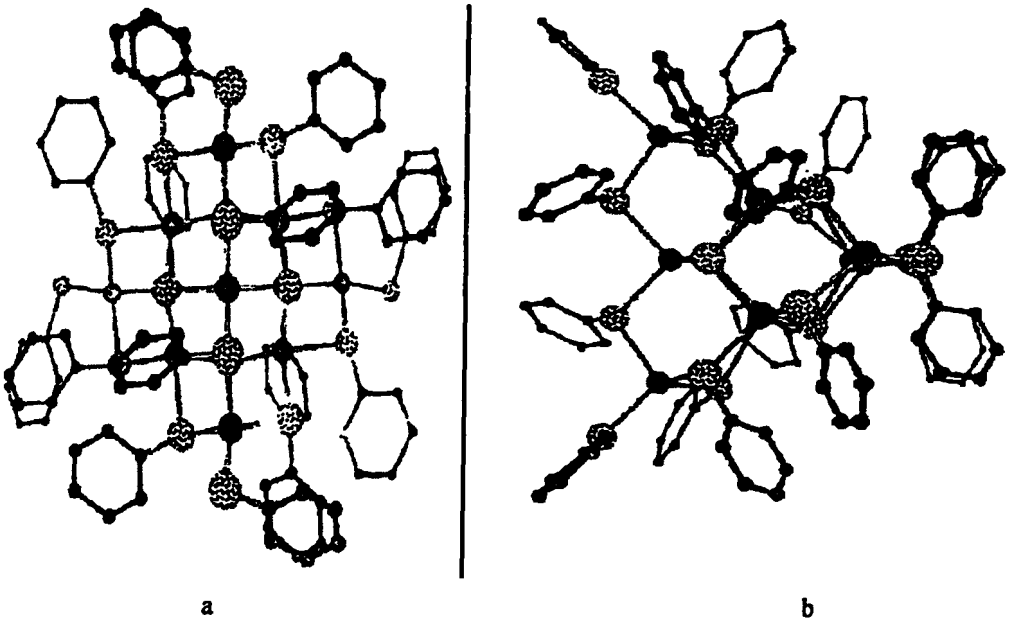

Fig. 1: Structure of $[Cd_{10}(\mu_3\text{-}S)_4(\mu\text{-}SPh)_{12}(SPh)_4]^{4-}$, the views are axial (a) and equatorial (b) relative to the $\bar{4}$ axis /6/

The remaining derivatives in Table 1 are polymeric. Colourless $Cd(mal)(H_2O)_2$ exists in two monoclinic isomeric forms /7,8/. In /7/ the structure contains two cadmium atoms and two maleate ligands, both pairs of which are crystallographically and chemically distinct. One cadmium atom is six–coordinate through four water molecules and two bridging maleate oxygen atoms, while the other is eight–coordinate, in distorted dodecahedral geometry, through four chelated carboxy groups from the two maleate ligands. The maleate ligands link cadmium atoms into a three-dimensional polymer, which is further strengthened by extensive hydrogen bonding through the water molecules.

In contrast, in /8/ the structure of $Cd(mal).(H_2O)_2$ contains only one type of distorted octahedrally coordinated Cd(II) atom (CdO_6). The four O atoms in each maleate anion bond to three symmetry-related Cd(II) atoms. The bidentate carboxylate groups coordinates asymmetrically to the metal, with the mean Cd – O bond distances of 2.235(6) and 2.423(4) Å, respectively. Other derivatives contain complex anions of the composition $[CdCl_4]^{2-}$ /9,10/ and $[CdCl_3]^-$ /11-14/. All cadmium centres are hexacoordinated and held together in a polymeric form by doubly (former case) or triply (latter case) bridging chloride atoms. $(Me_3NH)[CdCl_3]$ has been studied at several different temperature at 173, 295, 346, 355, 375, and 389 K, during which an orthorhombic – hexagonal phase change was observed (Table 1).

Colourless $Cd(\mu\text{-}\eta^2\text{-}NCS)_2(ba)_2$ /15,16/ exists in two monoclinic isomeric forms. In both forms NCS groups serve as bridges between $Cd(ba)_2$ units. The Cd – L bond distances are much longer when the NCS ligand binds via the softer S atom rather than the harder N atom. The mean Cd – NCS vs Cd – SCN distances are 2.372 vs 2.754 Å in one isomer /15/ and 2.319 vs 2.753 Å in the other one /16/. Two unidentate benzylamine ligands complete in each isomer a hexa – coordination (CdN_4S_2) about each Cd(II) atom, with mean Cd – N bond distances of 2.294 and 2.322 Å, respectively.

Colourless $Cd(\mu\text{-}4\text{-}H_2Nbz)_2(H_2O)_3$ exists in two isomeric forms, triclinic /17/ and monoclinic /18/. Each Cd(II) atom has a pentagonal bipyramid arrangement. The pentagonal plane around each Cd(II) atom is created by four O atoms of bidentate carboxylate groups of two 4-aminobenzoate anions and one O atom of water molecule which completes the plane. Apical positions are occupied by N atoms of two 4-aminobenzoates from the neighboring molecules, forming a polymeric chain. Two water molecules are not coordinated to the metal atom, but are bound by hydrogen bonds.

Inspection of the data in Table 1 reveals that one example exists in three isomeric forms and five in two isomeric forms with homo– as well as hetero– crystal classes. All three isomeric forms belong to the homo–tetragonal class /5,6/ and two isomeric forms to the homo– monoclinic /7,8,15,16/. The remaining examples differ from each other not only by degree of distortion but also by crystal class. In two of these one isomer is orthorhombic and the other monoclinic, /4,9/ in another one isomer is orthorhombic and the other hexagonal /10-14/. Finally there is a derivative with one isomer triclinic /17/ and the other monoclinic /18/.

Colourless $(NMe_4)_4[Cd_{10}(\mu_3\text{-}S)_4(\mu\text{-}SPh)_{12}(SPh)_4]$ /5,6/ exists in three (tetragonal) isomeric forms. Each Cd(II) atom has a tetrahedral arrangement (CdS_4) with a different degree of distortion. Remainders exist in two isomeric forms. In /4,7,8/ each Cd(II) atom is six–coordinate (CdO_6). In /9-14/ six chloride anions create a pseudo-octahedral arrangement around each Cd(II) atom ($CdCl_6$) /15,16/ each Cd(II) atom is also six – coordinate with the chromophore CdN_4S_2. A pentagonal bipyramidal (CdO_5N_2) environment was found in /17,18/.

2.2 Independent molecules

There are twenty-three derivatives which contain two crystallographically independent molecules within the same crystal /19-34, 37-42/ Two derivatives contain three such molecules /35,36/. Their crystallographic and structural data are gathered in Table 2. There are nineteen monomeric derivatives /19-35/, two dimeric /37,38/, one trimeric /39/, and the remaining ones are polymeric /40-42/ In the series of monomeric cadmium(II) complexes, the inner coordination sphere around Cd(II) atoms are with chromophores: CdI_4 /19/, $CdSe_4$ /20/, CdN_2I_2 /21/, CdO_6 /4,22/, CdN_6 /24,26,35/, CdO_4N_2 /27/, CdN_4O_2 /28,36/, CdN_4S_2 /29/, CdS_4N_2/30/, CdN_4OS /31/, CdO_7 /321/, CdO_5N_2 /33/, CdO_8 /7/, and CdO_6I_2 /34/.

The structure of colourless derivative /19/ contains well-separated $[Sr(H_2O)_8]^{2+}$ cations and $[CdI_4]^{2-}$ anions. In the anion the Cd(II) atom is tetrahedrally coordinated by four unidentate iodide anions, with the mean Cd – I bond distances 2.782(2) Å in molecule 1 and 2.775(2) Å in molecule 2. The six "tetrahedral angles" fall in the narrow range 100.4(1) – 127.75(7)° (molecule 1) and 103.1(1) – 124.48(7)° (molecule 2). The former molecule is somewhat less crowded and more distorted than the latter one.

Black derivative /20/ contains besides $[Ba(18\text{-crown-}6)(dmf)_4]^{2+}$ cation a $[Cd(\eta^2\text{-}Se_4)_2]^{2-}$ anion. A tetrahedral structure around the Cd(II) atom is created by two bidentate Se_4 ligands. The mean Cd – Se bond distances and the mean five – membered metallocyclic rings are 2.646(2) Å and 107.0(1)° (molecule 1) and 2.651(2) Å and 102.63(6)° (molecule 2).

In white $Cd(\eta^2\text{-bsn})I_2$ /21/ a homo – bidentate bsn ligand (N,N) with two iodide ligands form a tetrahedral environment about each Cd(II) atom (CdN_2I_2). The mean Cd – N and Cd – I bond distances, molecule 1 vs molecule 2, are: 2.264 and 2.699 Å vs 2.266 and 2.702 Å. Five of the six "tetrahedral angles" fall in the narrow range 101.8 – 122.4 ° and 102.7 – 120.0°, while the angle which is a part of the six – membered metallocycles (N – Cd – N) is significantly smaller (90.96(65) vs 90.46(53)°).

There are two colourless derivatives, $K[Cd(\eta^2\text{-acac})_3]\cdot H_2O$ /22/ and $Cd(\eta^6\text{-inomycin})$ /4/, in which each Cd(II) atom is hexacoordinated (CdO_6). In the former, three bidentate acetylacetonate ligands create an octahedral arrangement about the Cd(II) atom, and in the latter this is obtained by a hexadentate inomycin ligand. The derivatives contain two crystallographically independent molecules which differ by degree of distortion. The mean Cd – O bond distances molecule 1 vs molecule 2, are 2.291 vs 2.275 Å /22/ and 2.30 vs 2.40 Å /4/. The values of the T parameter ($T = R_S/R_L$) /23/ for $[Cd(\eta^2\text{-acac})_3]$, indicating the degree of tetragonal distortion around the cadmium(II) centers, molecule 1 vs molecule 2, are 0.979 vs 0.982, which means that the molecule 1 is somewhat more distorted than the molecule 2.

In another four colourless derivatives, $[Cd(\eta^2\text{-en})_3]I_2$ /24/, $Cd\{\eta^3\text{-}HB(3,5\text{-}Me_2pz)_3\}_2$ /25/, $[Cd(\eta^3\text{-tac})_2](ClO_4)$ /26/, and $[Cd(\eta^3\text{-tac})_2](BPh_4)_2$ /26/, six N donor atoms of the respective ligands create six–coordination around each Cd(II) atom. Each derivative contains two crystalographically independent molecules, again differing by degree of distortion (Table 2).

In yellow $Cd(\eta^2\text{-}C_6H_5O_3)_2(\eta^2\text{-}Me_4en)$ /27/, a pair of homo-(O,O)-bidentate 3-hydroxy-2-methyl-4-pyrone anions with a homo-(N,N)- bidentate Me_4en ligand, create an octahedral coordination about Cd(II) atom (CdO_4N_2). Two crystallographically independent molecules differ by degree of distortion (Table 2).

Table 2. Crystallographic and Structural Data for Cadmium(II) Compounds Containing Independent Molecules – Distortion Isomers[a]

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Cd – L [Å]	L – Cd – L [°]	Ref.
A: Monomers							
$[Sr(H_2O)_8][CdI_4]$ (colourless)	or Pnma 8	14.046(2) 18.411(5) 14.206(3)		CdI_4	I[b] 2.782(2,23)	I,I[b] 105.5(1,5.1) 127.75(7)	19
				CdI_4	I 2.775(2,31)	I,I 106.4(1,4.3) 124.48(7)	
{Ba(18-crown-6). $(dmf)_4][Cd(\eta^2\text{-}Se_4)_2]$ (black) (at 183 K)	m P2/a 4	20.219(12) 10.198(6) 22.708(4)	106.98(4)	$CdSe_4$	Se 2.646(2,5)	Se,Se 107.0(1,2)[c] 111.0(1,8.6)	20
				$CdSe_4$	Se 2.651(2,0)	Se,Se 102.63(6)[c] 111.3(1,7.4)	
$Cd(\eta^2\text{-bsn})I_2$ (white)	m $P2_1$ 8	17.055(5) 13.016(4) 13.563(4)	102.54(2)	CdN_2I_2	N 2.264(19,9) I 2.699(2,20)	N,N 90.96(65)[d] I,I 122.37(7) N,I 109.6(1,7.8)	21
				CdN_2I_2	N 2.226(16,4) I 2.702(2,14)	N,N 90.46(53)[d] I,I 120.01(7) N,I 110.5(1,7.8)	
$K[Cd(\eta^2\text{-acac})_3]\cdot H_2O$ (colourless)	m $P2_1/a$ 4	16.46(1) 14.051(6) 8.404(3)	101.60(3)	CdO_6	O 2.247(7)x2 2.303(7)x2 2.325(9)x2	O,O 80.1(3,2.3)[d] 85.4(3) 133.4(3,2.1)	22
				CdO_6	O 2.258(7)x2 2.264(7)x2 2.302(8)x2	O,O 80.9(3,2.1)[d] 84.9(3,1.4) 137.3(3,1)	
$Cd(\eta^6\text{-inomycin})$ (colourless)	m $P2_1$ 4	12.132(2) 33.991(14) 13.191(3)	116.0(0)	CdO_6	O 2.30(-,20)	O,O 84-177	4
				CdO_6	O 2.40(-,40)	O,O 76-162	

$[Cd(\eta^2\text{-en})_3]I_2$ (colourless)	tr P1 4	8.835(1) 14.294(2) 14.570(2)	107.15(1) 95.50(1) 100.97(1)	CdN_6 CdN_6	N 2.38(2,4) N 2.38(2,4)	N,N 75.3(6,1.5)[c] N,N 76.2(7,1.1)[c]	24
$Cd\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}_2$ (colourless)	trg R-3 2	10.423(4)	63.71(4)	CdN_6 CdN_6	N 2.31(1)x6 N 2.43(1)x6	N,N 80.1(3)[d] 97.3(3),180 N,N 90.0(8,3) 180	25
$[Cd(\eta^3\text{-tac})(ClO_4)_2$ (colourless)	tr P1 1	9.228(1) 9.533(1) 14.095(2)	80.45(1) 89.79(1) 62.45(1)	CdN_6 CdN_6	N 2.351(3)x2 2.362(3)x2 2.372(3)x2 N 2.308(3)x2 2.362(3)x2 2.382(3)x2	N,N 75.6(1,4)[c] 104.4(1,4) N,N 75.9(1,4)[c] 104.1(1,4)	26
$[Cd(\eta^3\text{-tac})(BPh_4)_2 \cdot$ dmso (colourless)	tr P1 1	11.298(2) 11.364(2) 13.936(2)	74.78(1) 71.05(1) 67.45(1)	CdN_6 CdN_6	N 2.315(5)x2 2.328(5)x2 2.413(6)x2 N 2.301(8)x2 2.372(8)x2 2.443(8)x2	N,N 76.0(2,6)[c] 104.0(2,6) N,N 74.7(3,1.5)[c] 105.3(3,1.5)	26
$Cd(\eta^2\text{-C}_6\text{H}_5\text{O}_3)_2(\eta^2\text{-}$ $\text{Me}_4\text{en})$ (yellow)	or Ibca 16	16.329(10) 15.911(8) 32.183(18)		CdO_4N_2 CdO_4N_2	O 2.237(8)x2 2.312(9)x2 N 2.351(15)x2 O 2.198(8)x2 2.346(10)x2 N 2.352(15)x2	O,O 74.2(3)[c] 100.8(3,3.0) N,N 76.0(8)[c] O,N 94.0(3,5.7) O,O 74.2(3)[c] 98.5(3,1.9) N,N 75.0(8)[c] O,N 94.7(4,1.6)	27

Table 2. continued 2

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Cd – L [Å]	L – Cd – L [°]	Ref.
$Cd(\eta^2\text{-}2,2'\text{-bpy})_2(NO_3)_2$ (colourless)	or Pcab 16	14.372(1) 35.134(2) 17.174(4)		CdN_4O_2	N 2.36(1,3) O_2NO 2.246(9) 2.43(1)	N,N 70.4(4,9)[c] 93.2(4,7.7) O,O 100.0(3) N,O 81.5-164.4(5)	28
				CdN_4O_2	N 2.38(1,5) O_2NO 2.42(1,1)	N,N 69.8(4,0)[c] 90.0(4,4.0) O,O 87.9(2) N,O 76.5-159.3(4)	
$Cd(py)_2(\eta^2\text{-}C_7H_4NS_2)_2$ (not given)	or Pccn 8	16.318(2) 16.515(2) 18.936(2)		CdN_4S_2	pyN 2.330(6)x2 η^2N 2.392(5)x2 η^2S 2.715(2)x2	N,N 92.7(2,4.5) 154.7(2,0) S,S 163.9(1) N,S 62.1(3,7)[e] 98.8(2,6.7)	29
				CdN_4S_2	pyN 2.337(6)x2 η^2N 2.450(5)x2 η^2S 2.696(2)x2	N,N 92.4(2,9.6) 155.4(2,0) S,S 163.8(2) N,S 62.1(1,0)[e] 98.5(2,4.5)	
$Cd(\eta^2\text{-}Et_2dtc)_2(\eta^2\text{-phen})$ (yellow)	tr P1 4	11.052(2) 15.185(2) 16.978(3)	106.43(1) 99.84(1) 101.35(1)	CdS_4N_2	S 2.603(4,8) 2.731(4,14) N 2.40(1,2)	S,S 67.2(1,1)[e] 105.1(1,11.8) 154.6(1) N,N 67.6(3)[c] S,N 83.1-140.6(3)	30
				CdS_4N_2	S 2.631(4,4) 2.717(4,50) N 2.41(2,2)	S,S 67.4(1,1.0)[e] 107.5(2,13.7) 154.9(2) N,N 68.0(4)[c] S,N 83.5-142.3(3)	

$[Cd(\eta^2\text{-bpy})_2(\eta^2\text{-pt})]\cdot ClO_4\cdot 0.5bpy$ (not given)	m $P2_1/c$ 8	16.491(1) 23.536(1) 14.455(1)	95.80(2)	CdN_4OS CdN_4OS	N 2.36(2,3) ptO 2.28(1) ptS 2.532(7) N 2.37(2,2) ptO 2.28(1) ptS 2.525(6)	N,N 69.0(6,9)[c] 95.0(6,4.4) 152.3(6) N,O 93.5(5,9.1) 163.7(5) N,S 103.2(5,4.9) 153.4(4) O,S 76.7(5)[c] N,N 70.3(6,5)[c] 94.5(6,5.5) 153.2(6) N,O 93.2(6,9.5) 162.5(6) N,S 102.6(4,3.4) 155.6(4) O,S 76.8(4)[c]	31
$Cd(C_7H_8O_2)_3(NO_3)_2$ (colourless)	m $P2_1/n$ 8	19.372(5) 11.345(4) 23.023(5)	93.77(5)	CdO_7 CdO_7	O_2NO_{eq} 2.401(5,43) O_{eq} 2.287(4) O_{ap} 2.287(4,6) O_2NO_{eq} 2.412(5,55) O_{eq} 2.282(4) O_{ap} 2.277(4,10)	O,O not given O,O not given	32
$Cd(dmpzeo)(NO_3)_2$ (colourless)	tr P1 4	14.854(8) 16.672(8) 9.112(3)	103.09(7) 93.13(8) 113.40(8)	CdO_5N_2 CdO_5N_2	O_2NO_{eq} 2.428(3,13) O_{eq} 2.595(2) N_{ap} 2.277(2,0) O_2NO_{eq} 2.459(2,11) O_{eq} 2.544(2) N_{ap} 2.248(2,1)	O,O 52.7(1,1)[e] 73.3-144.5(1) N,N 152.5(1) O,O 52.0(1,2)[e] 75.1-143.7(1) N,N 155.4(1)	33

Table 2. continued 3

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Cd – L [Å]	L – Cd – L [°]	Ref.
Cd(18-crown-6)I_2 (not given)	or Pnma 8	16.563(3) 27.996(5) 8.382(2)		CdO_6I_2	O_{eq} 2.76(1,2) I_{ap} 2.693(1,0)	O,O 60.3(3,5)[c] I,I 180.0 O,I 91.6(2,4.1)	34
				CdO_6I_2	O_{eq} 2.77(1,8) I_{ap} 2.691(2,7)	O,O 60.3(3,4)[c] I,I 177.7(1) O,I 90.0(3,5.7)	
[Cd(4-Mepy)$_4$(NCS)$_2$]· ·0.67(4- Mepy)·0.35 H_2O (colourless)	tr P1 3	17.726(4) 16.942(3) 11.262(4)	76.83(3) 115.06(2) 122.50(2)	CdN_6	pyN 2.40(3,6) SCN 2.34(3,3)	N,N not given	35
				CdN_6	pyN 2.46(3,8) SCN 2.21(3,8)		
				CdN_6	pyN 2.46(3,24) SCN 2.30(3,1)		
[Cd(tmtact)(NO_3)]$_2$ [Cd$(NO_3)_4$] (white)	m C2/c ?	53.360(13) 10.248(6) 31.938(7)	119.51(2)	CdN_4O_2	N 2.38(2,2) O 2.44(2,5)	N,N 89.7-177.3(1) O,O 51.6(6)[e] N,O 89.9(7,6.9)	36
				CdN_4O_2	N 2.39(2,2) O 2.46(2,5)	N,N 90.0-177.1(8) O,O 52.1(5)[e] N,O 89.7(6,4.5)	
				CdN_4O_2	N 2.40(3,7) O 2.43(2,3)	N,N 87.8-174.2(1) O,O 51.9(6)[e] N,O 90.1(8,2.2)	
				CdO_8	O 2.40(2,20)	O,O 50.9(9,3.2)[e]	

B: Di- and Trimers							
$[Cd(\mu\text{-mtt})_2(dmso)]_2$ (colourless)	tr P1 2	11.529(4) 12.995(5) 22.804(8)	106.4(8) 92.59(2) 94.68(2)	CdS_5O CdS_5O	μS 2.652(2,16) S 2.507(2) 2.890(3,85) O 2.358(2) μS 2.655(2,1) S 2.518(2) 2.866(3,90) O 2.360(5)	S,S 74.02(6)[c] 85.5-178.73(6) S,O 95.0(1) 146.1(1) S,S 72.7(1,16)[c] 85.0-177.62(6) S,O 78.4(1)[c] 97.6(1,2.1) 150.70(16)	37
$[Cd(\eta^2\text{-}Ph_2PC_2H_4NEt_2)(\mu\text{-}Cl)Cl]_2$ (colourless) at 138(2) K	m $P2_1/c$ 4	19.944(10) 12.247(4) 15.959(9)	96.10(3)	$CdCl_3NP$ $CdCl_3NP$	μCl 2.4835(11) 2.7788(12) Cl 2.4277(12) N 2.503(4) P 2.5634(12) μCl 2.502(12) 2.7797(12) Cl 2.4220(14) N 2.507(4) P 2.6168(12)	Cl,Cl 103.7(1,8.8) Cl,N 96.7(1,3) 166.57(9) Cl,P 123.8(1,1.9) N,P 77.56(9)[c] Cl,Cl 105.7(1,14.0) Cl,N 94.9(1,2.9) 170.28(9) Cl,P 120.1(1,4.3) N,P 76.11(9)[c]	38
$[Cd_3(\mu\text{-}Pr^i_3C_6H_2S)_4(Pr^i_3C_6H_2SH)_2\text{-}(Pr^i_3C_6H_2SH)]\cdot MeOH\cdot 7\,H_2O$ (colourless)	tr P1 4	19.792(10) 20.508(12) 33.97(2)	85.81(5) 86.77(5) 85.12(4)	CdS_3 CdS_4 (x2) CdS_3 CdS_4 (x2)	μS 2.478(9,18) S 2.429(11) μS 2.560(9,21) 2.647(9,23) S 2.420(10,7) μS 2.474(9,17) S 2.420(11) μS 2.554(9,33) 2.628(9,12) S 2.424(10,4)	μS,μS 120.8(3) μS,S 119.3(4,9.2) μS,μS 89.4(3,7.9) μS,S 125.5(3,7.6) μS,μS 119.2(3) μS,S 120.3(4,9.8) μS,μS 125.0(3,7.3) μS,S 90.0(3,10.1)	39

Table 2. continued 4.

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Cd – L [Å]	L – Cd – L [°]	Ref.
C:POLYMERS							
$Cd(\mu\text{-}4\text{-}MeC_6H_4S)_2$ (colourless)	m $P2_1/2$ 16	27.196(9) 15.722(5) 37.046(13)	123.03(1)	CdS_4 CdS_4	μS 2.544(3,25) μS 2.544(3,28)	μS,μS 108.8(-,15)	40
$Cd(\mu\text{-}I)_2(dmso)$ (not given)	m $P2_1/c$ 16	8.850(16) 26.950(10) 15.533(7)	99.06(4)	CdI_4 CdI_4O_2 CdI_4 CdI_4O_2	μI 2.787(3,8) μI 3.027(3,68) O 2.253(21,6) μI 2.785(3,13) μI 3.024(3,52) O 2.244(19,20)	μI,μI not given	41
$Cd(tse)_2(SO_4)$ (colourless)	m C2/c 8	27.962(14) 6.564(3) 15.908(9)	126.6(6)	$CdO_2N_2S_2$ (*cis*) $CdO_2N_2S_2$ (*trans*)	O_3SO 2.413(3,0) N 2.367(5,0) S 2.545(2,0) O_3SO 2.525(5,0) N 2.367(4,0) S 2.514(2,0)	O,O 169.7(1) N,N 94.3(2) S,S 110.6(1) N,S 77.9(1)[e] N,S 79.2(1)[e]	42

Footnotes: a) When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e. s. d. , the second is the maximum deviation from the mean.
b) The chemical identity of the coordinated atom or ligand is specified in these columns.
c) Five-member metallocyclic ring.
d) Six-member metallocyclic ring.
e) Four-member metallocyclic ring.

In colourless $Cd(\eta^2\text{-bpy})_2(NO_3)_2$ /28/, three bidentate ligands (two 2,2'-bipyridine with one nitrate) create an octahedral arrangement around each Cd(II) atom (CdN_4O_2) with the mean Cd – N and Cd – O bond distances (molecule 1 vs molecule2), 2.36 and 2.338 Å vs 2.38 and 2.42 Å.

An octahedral arrangement around each Cd(II) atom in $Cd(py)_2(\eta^2\text{-}C_7H_4NS)_2$ /29/, which contains two crystallographically independent molecules, is created by two unidentate pyridine molecules and two hetero-(N,S)-bidentate benzothiazole-2-thiolate anions (CdN_4S_2). The mean Cd – N(py), Cd – N and Cd – S bond distances are 2.330(6), 2.392(5) and 2.715(2) Å in molecule 1 and 2.337(6), 2.450(5) and 2.696(2) Å in molecule 2. The former molecule is somewhat more crowded than the latter one, the sum of Cd – L(x6) bond distances is 14.87 vs 14.97 Å.

Two homo – S,S – bidentate Et_2dtc anions with one homo – N,N – bidentate 1,10-phenanthroline ligand form an octahedral arrangement around each Cd atom (CdS_4N_2| in a yellow derivative /30/. Two crystallographically independent molecules are differing by degree of distortion (Table 2).

In another derivative, $[Cd(\eta^2\text{-bpy})_2(\eta^2\text{-pt})]_2ClO_4 \cdot 0.5bpy$ /31/, an octahedral coordination around each Cd(II) atom is created by two homo-N,N- 2,2'-bipyridine ligands and hetero-O,S-bidentate N-oxopyridine-2-thiolate (CdN_4OS). Two independent molecules differ by degree of distortion.

There are two colourless $Cd(C_7H_8O_2)_3(NO_3)_2$ /32/ and $Cd(dmpzeo)(NO_3)_2$ /33/ in which each Cd(II) atom is hepta-coordinated. In both derivatives the geometry around Cd(II) atoms is pentagonal bipyramidal with the chromophores CdO_7 /32/ and CdO_5N_2 /33/. Each derivative contains two crystallographically independent molecules. From the data in Table 2 it is seen that the derivatives have shorter mean Cd – L_{ap} than mean Cd – L_{eq} bond distances, with the values in /32/ 2.344 vs 2.287 Å (molecule 1) and 2.347 vs 2.277 Å (molecule 2); and in /33/ the respective values are 2.512 vs 2.277 Å and 2.502 vs 2.248 Å. This is in accordance with the concept that the apical sites of a pentagonal bipyramid are less sterically hindered than the five equatorial sites.

In $Cd(\eta^6\text{-crown-6})I_2$ /34/ the Cd(II) atom has a hexagonal bipyramidal environment. The apical sites are occupied by iodine atoms while the equatorial sites are occupied by a hexadentate ligand (CdO_6I_2). Two independent molecules differ by degree of distortion (Table 2).

In two examples, $[Cd(4\text{-Mepy})_4(NCS)_2] \cdot 0.67(4\text{-Mepy}) \cdot 0.35H_2O$ /35/ and $[Cd(\eta^4\text{-tmtact})(\eta^2\text{-}NO_3)]_2[Cd(NO_3)_4]$ /36/, there are three crystallographically independent molecules. In the former each Cd(II) atom has an octahedral coordination, created by unidentate (four 4-Mepy and two NCS) ligands (CdN_6). The sum of all Cd – N bond distances are 14.28 Å (molecule 1), 14.25 Å (molecule 2) and 14.44 Å (molecule 3) which indicates that from this trinity the most bulky is molecule 3 and the less bulky is molecule 2, while the molecule 1 lies between them.

X–ray analysis of the latter /36/ shows that the complex $[Cd(\eta^4\text{-tmtact})(\eta^2\text{-}NO_3)_2]^+$ cations and $[Cd(NO_3)_4]^{2-}$ anions are well-separated. In the complex cation each Cd(II) atom has a pseudo–octahedral environment (CdN_4O_2). The mean value of the sum of six Cd – L bond distances increases in the order: 14.40 Å (molecule 1) < 14.46 Å (molecule 3) < 14.48 Å (molecule 2). The anions have the classic tetranitrato arrangement, with dodecahedral coordination geometry (CdO_8) with the mean Cd – O bond distance of 2.40 Å (Table 2).

There are dimeric derivatives, $[Cd(\mu\text{-mtf})_2(dmso)]_2$ /37/ and $[Cd(\eta^2\text{-}Ph_2PC_2H_4NEt_2)(\mu\text{-}Cl)Cl]_2$ /38/, which contain two crystallographically independent dimeric molecules (Table 2B). In the former triclinic derivative /37/, two sulphur *cis*-1-methyl- thiostilbene-2-thiolate ligands serve as bridges between Cd(dmso) units. A pseudo–octahedral environment about each Cd(II) atom is created (CdS_5O) (Fig. 2). The centrosymmetric dimer form is doubly μS – bridged, in which each Cd(II) atom is coordinated to five sulphur atoms of the mtf ligands, and one oxygen atom of dmso ligand. The Cd_2S_4 moiety is approximately rectangular, although Cd(2) is displaced by 0.426 Å out of S(1) Cd(1) S(1a) plane. The two coordinate terminal Cd – S bonds, Cd(1) – S(2) and Cd(1) – S(4) of 2.8045(2) and 2.976(3) Å (in one dimer) and 2.776(3) and 2.956(3) Å (in the other one), are relatively long, but the angles of the bonds around these sulphur atoms are rarely tetrahedral, consistent with the presence of genuine coordination to cadmium. The mean Cd(1) – S – Cd(2) angles are 88.84(7)° and 87.47(7)°, respectively. The sum values of the six Cd – L bond distances are 15.95 Å (in dimer 1) and 15.92 Å (in dimer 2), which indicates that the latter dimer is somewhat less crowded than the former one.

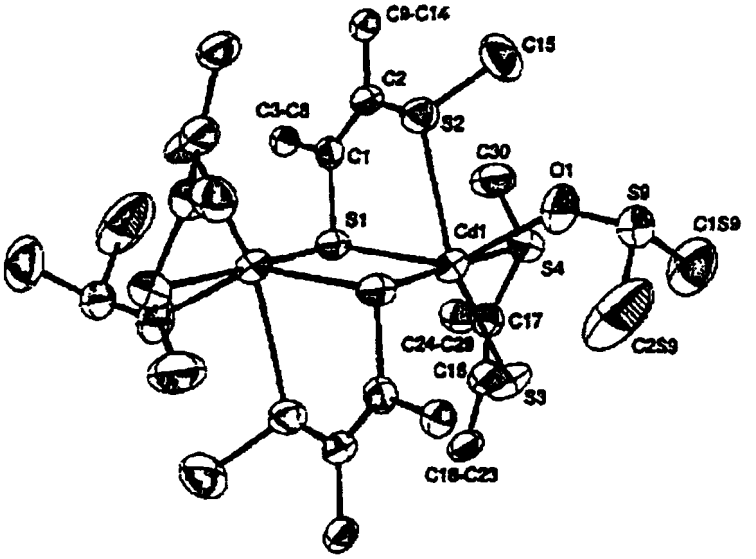

Fig. 2: Structure of $[Cd(\mu\text{-mtt})_2(dmso)]_2$ /37/

In /38/ two chlorine atoms serve as bridges between two $Cd(\eta^2\text{-}Ph_2PC_2H_4NEt_2)Cl_2$ moieties. The Cd . . . Cd separation of 3.875 Å (in dimer 1) and 3.934 Å (in dimer 2) rules out a direct bond. Each Cd(II) atom has a trigonal bipyramidal arrangement ($CdCl_3NP$). Two chlorine atoms with the P atom create a plane and the remaining chlorine with the N atom occupy apical positions. The mean Cd – Cl – Cd and μCl – Cd – μCl bond angles (dimer 1 vs dimer 2) are 94.69(4) and 85.31(4)° vs 95.73(4) and 84.27(4)°. The mean values of all five Cd – L bond distances are 12.76 and 12.83 Å, respectively. In the former dimer each Cd(II) atom is somewhat more crowded than that in the latter.

There is one trimer, $Cd_3(\mu\text{-}Pr^i_3C_6H_2S)_4(Pr^i_3C_6H_2S)_2(Pr^i_3C_6H_2SH)$ /39/, which contains two

crystallographically independent trimer units. This is the only example of trimers in the series. The structure of the trimer is shown in Fig. 3. The three Cd(II) atoms are coordinated by six thiolate $(RS)^-$ ligands and one thio (RSH) ligand. Three of them are terminal and four are double bridged, in such a way that two of the Cd(II) atoms have tetrahedral geometry (CdS_4) while the remaining one is trigonal planar (CdS_3) (Table 2B). The mean Cd – S (bridge) bond distances are longer than the corresponding terminal distances. Noticeably, while the mean Cd – S (bridge) bond distances for CdS_3 are much shorter than the corresponding distances for CdS_4 (2.478 vs 2.604 Å in one trimer, and 2.474 vs 2.591Å in another trimer), the mean Cd – S (terminal) bond distances are nearly equal (2.429 vs 2.420 Å and 2.420 vs 2.424 Å), respectively. The mean Cd – S – Cd bridge angles in CdS_3 are more open (108.7 and 111.0°) than those in CdS_4 (96.3 and 96.5°), respectively.

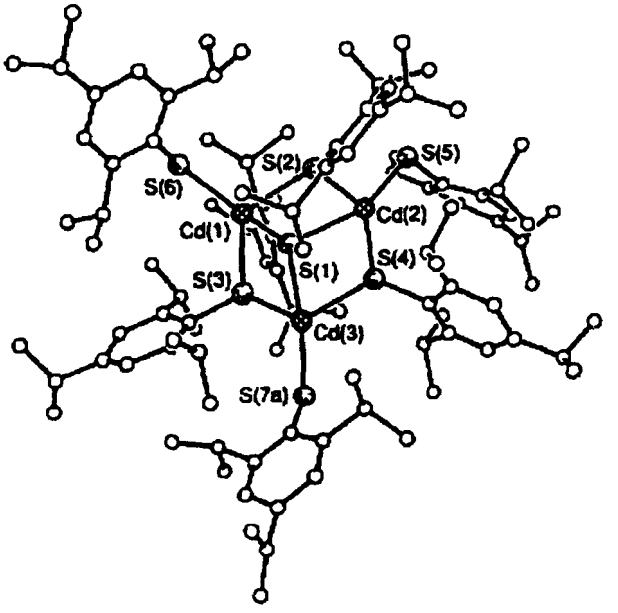

Fig. 3: Structure of $[Cd_3(\mu\text{-}Pr^i{}_3C_6H_2S)_4(Pr^i{}_3C_6H_2S)_2(Pr^i{}_3C_6H_2SH)]$ /39/

There are three polymeric derivatives /40-42/ which contain two crystallographically independent molecules (Table 2C). The structure of colourless $Cd(\mu\text{-}4\text{-}MeC_6H_4S)_2$ /40/ is shown in Fig. 4. This compound contains adamantanoid cage units, linked to four neighbours by doubly-bridging thiolate ligand in a three – dimensional nonmolecular lattice, and can be formulated as $\infty^3[(\mu\text{-}SC_6H_4Me)_6Cd_4(\mu\text{-}SC_6H_4Me)_{4/2}]$. The linkage pattern involves closed four-, six-, and eight- membered rings of tetrahedra, resembling microporous zeolite lattices. There exist very large centrosymmetric cavities in the Cd – S array, surrounded by 12 adamantanoid cages whose centroids constitute a *trans* truncated octahedron. Channels surrounded by eight – membered rings also exist in the lattice. The cavities are lined with 44 S atoms connected by 32 Cd atoms, contain 10 ligand substituents and are connected through four– and six– membered rings to other cavities.

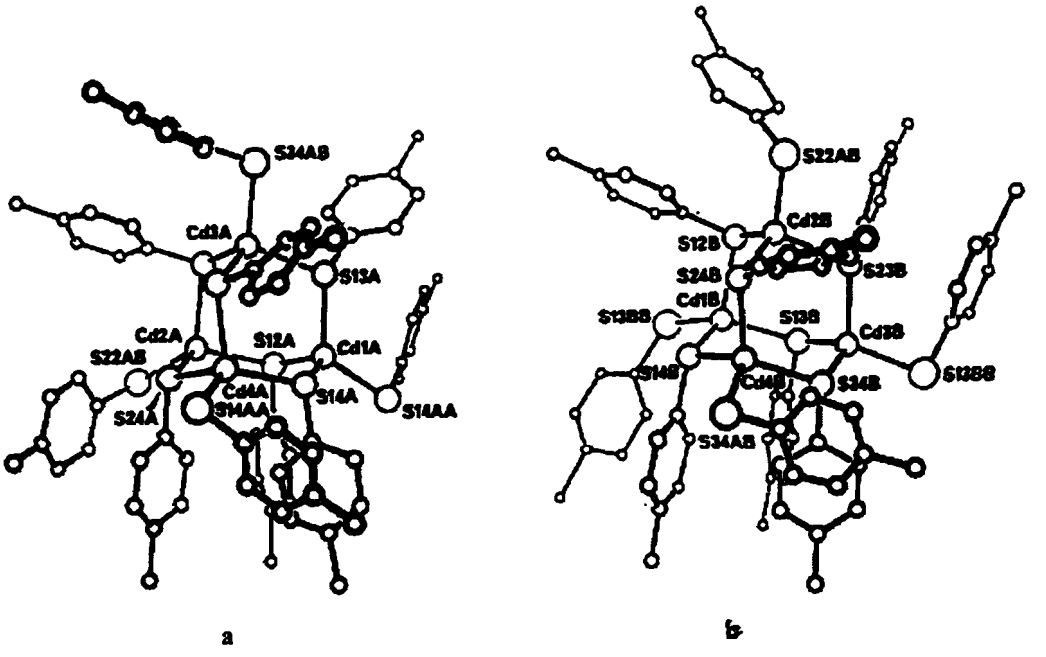

Fig. 4: Structure of two independent molecules, $Cd(\mu\text{-}4\text{-}MeC_6H_4S)_2$ /40/

The structure of $Cd(\mu\text{-}I)_2(dmso)$ /41/ consists of polymeric chains with cadmium centres bridged by iodine atoms, with alternate four coordination (CdI_4) and six coordination (CdI_4O_2). The mean Cd – I (bridge) bond distances, CdI_4 vs CdI_4O_2, are 2.787 vs 3.027 Å (in molecule 1) and 2.785 vs 3.024 Å (in molecule 2). The mean Cd – O bond distances are 2.253 vs 2.244 Å.

A colourless crystal of $Cd(tsc)_2(SO_4)$ /42/ contains two independent units. In each of the units an octahedral arrangement about each Cd(II) atom is created by two oxygen atoms of sulphate groups as axial ligands. The hetero –N,S – chelating thiosemicarbazide ligands are coordinating in the plane *cis* in one unit and *trans* in the other. Each sulphate group uses two oxygen atoms for coordination, one to each type of cadmium, in such a way that chains are formed through the crystal. The remaining oxygen atoms in the sulphate groups are used for hydrogen bonding to the thiosemicarbazides. In this way the individual chains in the crystal are bound together in a very efficient network. The sum of all six (Cd – O (x2), Cd – N (x2) Cd – S (x2)) bond distances (Table 2C) are 14.654 Å (*cis*) and 14.812 Å (*trans*) indicates that the *cis* is somewhat more crowded that the *trans*, but *trans* is somewhat more distorted than the *cis*.

Inspection of the data in Table 2 reveals that the derivatives belong to the following crystal classes: monoclinic (x11) > triclinic (x8) > orthorhombic (x5) > trigonal (x1). In this series of distortion isomers the predominant arrangement about the cadmium(II) atom is octahedral (x11), with some examples of tetrahedral (x3), pentagonal – bipyramidal (x2), hexagonal – bipyramidal and dodecahedron, each (x1).

3. LIGAND ISOMERS

There are three colourless Cd(II) complexes which exhibit this type of isomerism: $Cd(\mu\text{-}\eta^2\text{-}NCS)_2(2\text{-}Mepy)_2$ /43/, $Cd(\mu\text{-}\eta^2\text{-}NCS)_2(3\text{-}Mepy)_2$/44/ and $Cd(\mu\text{-}\eta^2\text{-}NCS)(4\text{-}Mepy)_2$ /44/ (Tab. 3). In each, NCS groups serve as bridges between the $Cd(n\text{-}Mepy)_2$ moieties and form linear chains. The Cd – L distances are much longer when the NCS ligand binds via the softer S atom rather than the harder N atom. The mean Cd – NCS vs Cd – SCN distances are 2.276 vs 2.762 Å (with 2-Mepy), 2.300 vs 2.748 Å (3-Mepy), and 2.299 vs 2.719 Å (4-Mepy). Each Cd(II) atom has a pseudo – octahedral geometry with differing degrees of distortion. The mean Cd – N (n-Mepy) bond distance reflects the position of the methyl group and increases in the order: 2.359 Å (4-Me) < 2.369 Å (3-Me) <2.447 Å (2-Me). The value of T parameter ($T = R_S/R_L$) for $Cd(\mu\text{-}\eta^2\text{-}NCS)_2(n\text{-}Mepy)_2$, indicating the degree of tetragonal distortion about the Cd(II) centres, decreases in the order: n = 3-Mepy, 0.869 > 2-Mepy, 0.864 > 4-Mepy, 0.856. The Cd . . . Cd separations are over 5.8 Å and rule out a direct bond.

4. POLYMERISATION ISOMERS

White $Cd(dmpd)_2Br_2$ /45/ is a unique example consisting of equimolar molecular packing of monomers and dimers, both units lying on crystallographic inversion centres (Table 4) (Fig. 5). In the monomer, two

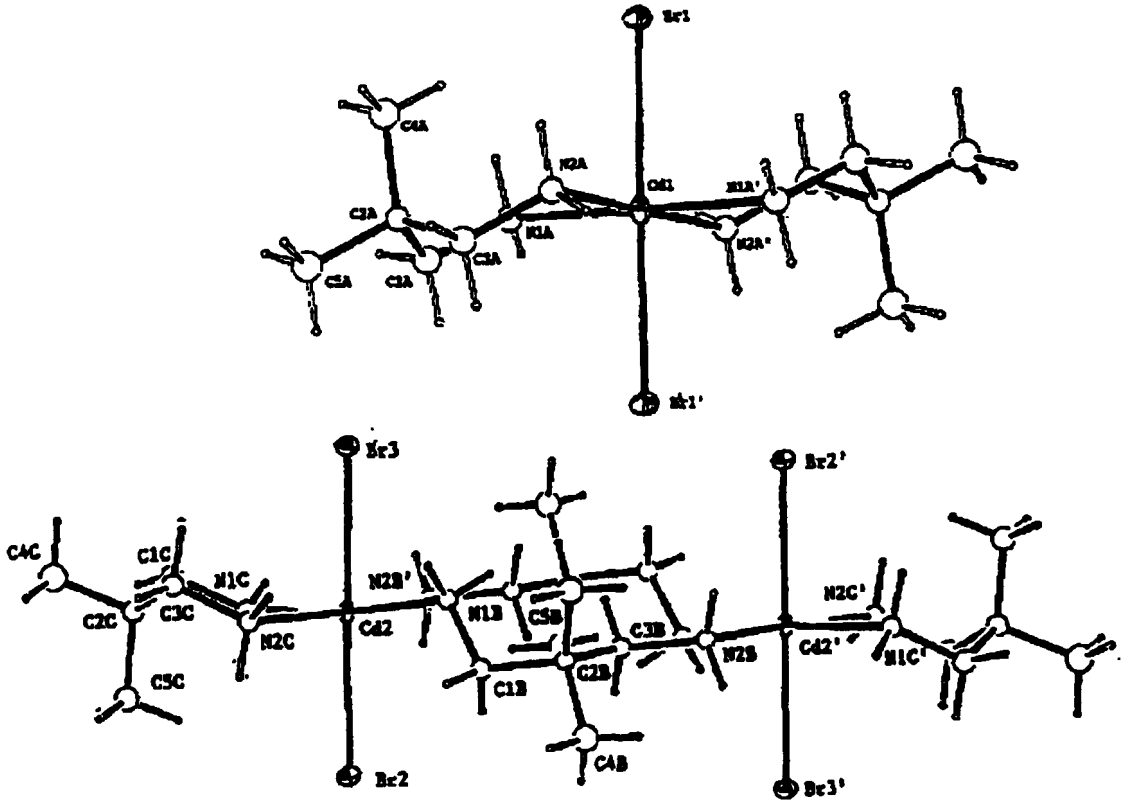

Fig. 5: Structure of $Cd(dmpd)_2Br_2$ (monomer and dimer) /45/

Table 3. Crystallographic and Structural Data for Cadmium(II) Complexes – Ligand Isomers[a]

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Cd – L	Cd . . . Cd [Å]	L – Cd – L [°]	Ref.
$Cd(\mu\text{-}\eta^2\text{-}NCS)_2(2\text{-}Mepy)_2$ (colourless)	tr P1 4	11.076(3) 18.478(8) 9.299(3)	104.60(3) 114.84(2) 81.12(3)	CdN_4S_2	μSCN[b] 2.276(5,32) μNCS 2.762(3,30) pyN 2.447(5,77)	5.835(2,1)	N,N[b] 91.5(1,6.2) S,S 86.24(8) N,S 89.7(1,7.9)	43
$Cd(\mu\text{-}\eta^2\text{-}NCS)_2(3\text{-}Mepy)_2$ (colourless)	tr P1 2	8.766(1) 16.655(4) 5.845(1)	91.40(2) 100.57(1) 92.52(1)	CdN_4S_2	μSCN 2.300(5,5) μNCS 2.748(2,11) pyN 2.369(1,8)	5.845(2)	N,N 90.0(1,1.6) S,S 176.25(5) N,S90.0(1,4.3)	43
$Cd(\mu\text{-}\eta^2\text{-}NCS)_2(4\text{-}Mepy)_2$ (colourless)	tr P1 4	11.323(4) 18.383(10) 9.284(5)	104.62(4) 114.26(3) 77.71(4)	CdN_4S_2	μSCN 2.299(4,8) μNCS2.719(2,3) pyN 2.359(5,9)	not given	N,N 90.0(1,2.7) S,S 91.56(3) N,S 90.9(1,7.4)	44

Footnotes: a) When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e. s. d. , the second is the maximum deviation from the mean.
b) The chemical identity of the coordinated atom or ligand is specified in these columns.

Table 4. Crystallographic and Structural Data for Cadmium(II) Complexes – Polymerisation Isomers[a]

Compound (colour)	Cryst. cl. Space gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Cd – L [Å]	L – Cd – L [°]	Ref.
$Cd(dmpd)_2Br_2$ (white)	tr P1 1	12.713(2) 16.592(2) 6.281(3)	91.22(2) 96.67(2) 78.72(2)	CdN_4Br_2 (monomer)	N[b] 2.303(7)x2 2.324(7)x2 Br 2.869(1)x2	N,N[b] 87.1(2)[c] 92.9(2) Br,Br not given N,Br 90.0(2,3.6)	45
				CdN_4Br_2 (dimer)	N 2.346(6,1) 2.374(6,11) Br 2.797(1,6)	N,N 86.6(2,3)[c] 93.5(2,1.2) Br,Br 178.86(4) N,Br 90.0(2,5.4)	

Footnotes: a) When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is e. s. d. , the second is the maximum deviation from the mean.
b) The chemical identity of the coordinated atom or ligand is specified in these columns.
c) Six-member metallocyclic ring.

homo–bidentate (N,N) dmpd ligands with a pair of bromine atoms create a tetragonal bipyramidal geometry around Cd(II) atom (CdN_4Br_2). The mean Cd – N and Cd – Br bond distances are 2.314 and 2.869 Å, respectively. The dimer consists of a pair of six-coordinate Cd(II) units connected by a 12 – membered metallocycle formed by the ambidentate dmpd ligands. On each metal centre the pseudo – octahedral coordination is completed by two bromine atoms, *trans* to each other, and a chelating dmpd ligands. Comparison of the Cd – N distances within the 12 – membered metallocycle and the six – membered indicates the former to have larger values (2.374 vs 2.345 Å). The same trend is also observed for the N – Cd – N angle (94.6(2) vs 86.2(29)°. The value of the T parameter ($T = R_S/R_L$) for CdN_4Br_2, indicating the degree of tetragonal distortion around the cadmium(II) centers, monomer vs dimer are 0.806 vs 0.844, which means that the monomer is somewhat more distorted than the dimer.

5. CONCLUSIONS

An analysis of over six hundred cadmium(II) coordination and organometallic compounds shows that some 8 % of them exist in isomeric forms /1/. Cadmium(II) complexes are for the most part colourless, but there are some examples of white, yellow and even black colour, some of which are due to ligand absorption and others due to charge – transfer bands. The lowest and highest coordination number found in the cadmium(II) isomers are four and eight, respectively. The frequency of occurrence increases in the order: eight- < seven- < five- < four- < six- coordinate. The most common are six-coordinate examples with variously tetragonally distorted arrangement. The four-coordinate examples are in variously distorted tetrahedral arrangements. The five-coordinate are trigonal bipyramid. The seven-coordinate are pentagonal – bipyramid and the eight-coordinate are dodecahedral and hexagonal bipyramidal. Consideration of the nuclearity of the isomers shows a range of possibilities: mono-, tri-, deca- and polymeric derivatives.

The "soft" behaviour of cadmium(II) atom is evident from the nature of the ligands commonly found and in particular the nature of the bonding. There are examples all the way from uni- to tetradentate and even hexadentate ligands, with several types of chromophores created by the same donor atoms and others with mixed donor atoms. There are unidentate ligands: OL, NL, Cl, SL, Se and I; homobidentate: OL, NL and SL; homoterdentate –NL; homotetradentate –NL and homohexadentate – OL. Heterobi – O plus S, N plus S and N plus P and heteroterdentate - 2 O plus N.

A summary of the mean Cd – L bond distances found in the distortion isomers (independent molecules), less vs more distorted, is given in Table 5. As can be seen, the most frequent ligands are S, N and O donors. In general the mean Cd – L bond distance elongates with an increased coordination number as expected. The mean Cd – L (terminal) bond distance is somewhat more covalent than that of Cd – L (bridge) bond distance. Bidentate as well as multidentate ligands are usually coordinated by several donor atoms.

The mean values of sum of Cd – L (xn) bond distances elongate with the sum of the covalent radii of donor atoms (xn) as well as with the increase of the coordination number, (less vs more distorted units) in the

Table 5.

Summary of the mean Cd – L bond distances [Å] in distortion isomers (independent molecules) less vs more distorted

coord. number 3	
- SL	2.420 vs 2.429
- μSL	2.474 vs 2.477
coord. number 4	
- N^2L	2.264 vs 2.266
- SL	2.439 vs 2.452
-μSL	2.574 vs 2.575
- μ_3SL	2.477 vs 2.482
- I	2.780 vs 2.784
- μI	2.785 vs 2.787
coord. number 5	
- N^2L	2.36 vs 2.37
- Cl	2.422 vs 2.428
$L^2 - O$	2.28 vs 2.28
$L^2 - S$	2.525 vs 2.532
$L^2 - N$	2.503 vs 2.507
$L^2 - P$	2.563 vs 2.617

coord. number 6	
- OL	2.306 vs 2.316
- NL	2.332 vs 2.341
- O^2L	2.355 vs 2.383
- N^2L	2.358 vs 2.38
- S^2L	2.686 vs 2.688
$L^2 - O$	2.28 vs 2.28
$L^2 - S$	2.325 vs 2.532
- $L^2 - N$	2.379 vs 2.409
- $L^2 - S$	2.630 vs 2.605
- N^3L	2.341 vs 2.384
- N^4L	2.38 vs 2.40
- O^6L	2.32 vs 2.40

coord. number 6	
- μOL	2.287 vs 2.287
- μCl	2.646 vs 2.648
- μS	2.652 vs 2.655
- μSCN	2.319 vs 2.372
- μNCS	2.753 vs 2.754
- μI	3.024 vs 3.027
coord. number 7	
- O^2L	2.372 vs 2.383
- L^3- ^2O	2.390 vs 2.389
- L^3- N	2.431 vs 2.437
coord. number 8	
- I	2.691 vs 2.693
- O^6L	2.76 vs 2.77

order: 9.23 vs 9.25 Å ([S_3 + $S_{4/2}$], 3.57 Å) < 9.91 vs 9.94 Å (N_2I_2, 4.10 Å) < 10.07 vs 10.115 Å (S_4, 4.08 Å) < 10.58 vs 10.61 Å (Se_4, 4.64 Å) < 11.10 vs 11.13 Å (I_4, 5.32 Å); 12.755 vs 12.83 Å (Cl_3NP, 4.98 Å) < 13.86 vs 13.88 Å ([I_4 + I_4O_2/2], 6.05 Å); 13.75 vs 14.12 Å (O_6, 4.08 Å) < 14.00 vs 14.32 Å (N_6, 4.50 Å) < 14.25 vs 14.285 Å (N_4OS, 4.75 Å) < 14.65 vs 14.81 Å ($O_2N_2S_2$, 5.00 Å < 15.92 vs 15.955 Å (S_5O, 5.83 Å); 16.465 vs 16.485 Å (O_7, 5.11Å) < 16.78 vs 16.80 Å (O_5N_2, 5.15 Å); and 21.145 vs 22.00 Å (O_6I_2, 7.04 Å).

As already mentioned, there are a variety of bi-, ter-, tetra- and even hexadentate ligands. Correspondingly, there is a variety of metallocyclic rings, and the effects of both steric and electronic factors can be seen from the mean values of the L – Cd – L interbond angles, which open in the sequence: 52.6 ° (-OCO-) < 62.1° (-NCS-) < 67.3 ° (-SCS-); 67.2 ° (-OC_2O-) < 73.3 ° (-SC_2S-) < 73.5 ° (-NC_2O-) < 76.9 ° (-NC_2P-) < 77.3 ° (-OC_2S-) < 78.5 °(-NC_2S-) < 104.8 ° (-$SeSe_2Se$-); and 80.6 ° (-OC_3O-) < 90.7 ° (-NC_3N-).

This review presents the first overview of structural data for cadmium(II) isomers. Interestingly, while in zinc(II) complex chemistry there exist only two types of isomers, distortion (96 %) and ligand isomers (4 %), in the cadmium(II) chemistry four types of isomers include: distortion (91.5 %), ligand (6.5 %), mixed isomerism (distortion and *cis – trans*) (1 %) and polymerisation isomerism (1 %). In general, the Cd – L bond distances are somewhat longer than those of Zn – L bond distances, however the L – Cd – L bond angles, are somewhat smaller than those of L – Zn – L bond angles, which corresponds well with the covalent radii of the respective metal atoms, 1.48 Å (Cd) vs 1.31 Å (Zn).

Despite the increasing availability of data retrieval systems, the tracing of relevant material is not always a straightforward task. Some data are obscured. The systematic analysis and correlation of structural data should serve to highlight both areas of interest and those requiring more investigation.

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6. REFERENCES

1. C. E. Holloway and M. Melník, *Rev. Inorg. Chem.* 1995, **18**, 431.
2. M. Melník, A. Valent and M. Kohútová, *Trends in Inorg. Chem.*, in press.
3. M. Melník, *Coord. Chem. Rev.* 1982, **47**, 239.
4. B. K. Toeplitz, A. I. Cohen, R. T. Funke, W. L. Parker and J. Z. Gougoutas, *J. Amer. Chem. Soc.* 1979, **101**, 3344.
5. A. Choy, D. Craig, I. Dance, and M. Scudder, *J. Chem. Soc., Chem. Commun.* **1984**, 6285.
6. G. S. H. Lee, K. J. Fischer. A. M. Vassallo, J. V. Hanna, and I. G. Dance, *Inorg. Chem.* 1993, **32**, 66.
7. M. L. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.* **1974**, 674.

8. A. Hempel, S. E. Hull, R. Ram, and M. P. Gupta, *Acta Crystallogr., Sec.B* 1979, **35**, 2215
9. R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Seliger, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahajnar, F. Milia, and G. Chaperis, *J. Chem. Phys.* 1979, **71**, 2118.
10. G. Chaperis and F. J. Zuniga, *Acta Crystallogr. Sect. B* 1980, **36**, 807.
11. G. Chaperis and F. J. Zuniga, *Acta Crystallogr. , Sect. B* 1988, **44**, 243.
12. S. Kashida and S. Sato, *J. Phys. Soc. Jpn.* 1985, **54**, 2934.
13. S. Kashida, Y. Ito, and S. Sato, *J. Solid State Chem.* 1987, **69**, 258.
14. B. Morosin, *Acta Crystallogr., Sect. B* 1972, **28**, 2303.
15. M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.* 1987, **60**, 4172.
16. A. Ouchi and M. Taniguchi, *Bull. Chem. Soc. Jpn.* 1988, **61**, 3347.
17. L. R. Amiraslanov, K. S. Mamedov, E. M. Movsumov, F. N. Musaev, A. I. Magerramov, and G. N. Nadzhapov, *Zh. Strukt. Khim.* 1979, **20**, 498; Engl. Ed., p. 420.
18. R. M. Turner, A. G. Charles, and E. L. Amma, *Cryst. Struc. Commun.* 1982, **11**, 241.
19. G. Tiele and D. Putzas, *Z. Naturforsch,*. 1988, 43b, 1224.
20. S. Magull, K. Dehnicke, and D. Fenske, *Z. Anorg. Allg. Chem.* 1992, **608**, 17.
21. P. Richard, A. Boulanger, J. F. Gueden, W. J. Kasoroski, and C. Bardeleau, *Acta Crystallogr., Sect. B* 1977, **33**, 1310.
22. T. M. Greaney, C. L. Raston, A. H. White and E. N. Maslen, *J. Chem. Soc., Dalton Trans.* 1975, 876.
23. J. Moncoľ, M. Múdra, P. Lönnecke, and M. Melník, *J. Coord. Chem.* 2004, **57**, 1065.
24. C. Mahadevan, M. Seshasayee, S. Sastry, and C. Subrahmanyan, *Z. Kristallogr.* 1985, **171**, 173.
25. W. R. McWhinnie, Z. Monsef – Mirzai, M. C. Perry, N. Shaikh, and T. A. Hamor, *Polyhedron* 1993, **12**, 1193.
26. H. Strastdeit, A. K. Duhme, M. Weber, and S. Pohl, *Acta Crystallogr., Sect. C* 1992, **48**, 437.
27. T. A. Annan, C. Peppe, and D. G. Tuck, *Can. J. Chem.* 1990, **68**, 423.
28. R. W. Turner, P. F. Rodesiler, and E. L. Amma, *Inorg. Chim. Acta* 1982, **66**, L13.
29. R. Baggio, M. T. Garland, and M. Perec, *J. Chem. Soc., Dalton Trans.* 1993, 3367.
30. C. Airoldi, S. F. De Oliveira, S. G. Ruggiero, and J. R. Lechat, *Inorg. Chim. Acta* 1990, **174**, 103.
31. J. Sanmartin, M. R. Bermejo, J. Romero, J. A. Garcia – Vaquez, A. Sousa, A. Brodbeck, A. Costiniras, W. Hiller, and J. Strähle, *Z. Naturforsch.* 1993, **48b**, 431.
32. A. Banerjee, C. J. Brown, P. C. Jain, and P. Gautam, *Acta Crystallogr , Sect. C* 1984, **40**, 1161.
33. E. A. H. Griffith, N. G. Charles, K. Lewinski, E. L. Amma, and P. F. Rodesiler, *Inorg. Chem.* 1987, **26**, 3983.
34. A. Hazell, *Acta Crystallogr., Sect. C* 1988, **44**, 88.
35. N. V. Pervukhina, N. V. Podberezskaya, V. V. Bakakin, N. V. Kislykin, G. M. Chekhova, and Y. A. Dyadin, *Zh. Strukt. Khim.* 1985, **26**, 120; Engl. Ed., p. 934.
36. N. W. Alcock, E. H. Curson, P. Moore, and C. Pierpont, *J. Chem. Soc., Dalton Trans.* 1984, 605.
37. H. K. Reddy, C. Zang, E. O. Schlemper, and G. N. Schrauzer, *Inorg. Chem.* 1992, **34**, 1673.

38. L. W. Houk, P. K. Sen Gupta, M. B. Hossain, and D. van der Helm, *Acta Crystallogr., Sect. B* 1982, **38**, 91.
39. K. Tang, A. Li, X. Jin, and Y. Tang, *J. Chem. Soc., Chem. Commun.* 1991, 1590; K. Tang, X. Yin, A. Li, Z. Li, and Y. Tang, *J. Coord. Chem.* 1994, **31**, 305.
40. I. G. Dance, R. G. Garbutt, D. C. Craig, and M. L. Scudder, *Inorg. Chem.*1987, **26** 4057.
41. M. Nieuwenhuyzen, Huo Wen, and C. J. Wilkins, *Z. Anorg. Allg. Chem.* 1992, **615**, 143.
42. E. Larsen and P. Trinderup, *Acta Chem. Scand., Ser A* . 1975, **29**, 481.
43. M. Taniguchi, Y. Sugita, and A.Ouchi, *Bull. Chem. Soc. Jpn.* 1987, **60**, 1321.
44. M. Taniguchi, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc, Jpn.* 1986, **59**, 2299.
45. M. Masciochi, M. Moret, A. Sironi, S. Bruni, F. Cariati, A. Pozzi, T. Manfredini, L. Menabue, and G. C. Pellacani, *Inorg. Chem.* 1992, **31**, 1401.