DALTON
FULL PAPER

Synthesis and crystal structure of thiocyanato or azido bridged one- or two-dimensional polymeric complexes of cadmium(II)

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Received 2nd June 2000, Accepted 31st July 2000

Four new polymeric complexes $[Cd(dmen)(SCN)_2]_n$ **1**, $[Cd(deen)(SCN)_2]_n$ **2**, $[Cd(dmen)(N_3)_2]_n$ **3** and $[Cd(deen)(N_3)_2]_n$ **4** (dmen = *N*,*N*-dimethylethylenediamine and deen = *N*,*N*-diethylethylenediamine) have been synthesized and characterized by single crystal X-ray diffraction. The various arrangements of thiocyanate anions give a 2-D polynuclear chain of pseudo sixteen membered rings for **1** and a 1-D polynuclear chain of eight membered rings for **2**. The 2-D polymeric sheets of complexes **3** and **4** involve the formation of two different rings, one a twenty membered zigzag ring and the other a four membered square ring. The co-ordination environment of the cadmium atom in all the complexes is distorted octahedral. In the azido-bridged complexes the cadmium(II) ions are linked both by end-on and end-to-end co-ordination, whereas in the thiocyanato-bridged complexes the cadmium(II) ions are bridged only by end-to-end co-ordination.

Introduction

The current surge of research activity in the area of co-ordination polymers has been motivated by the ability of metal–ligand co-ordination to provide a facile approach to the controlled assembly of one-, two-, or three-dimensional extended networks. The crystal engineering of co-ordination polymers with inner cavities or channels of desired size has been achieved recently by using suitable bidentate ligands.[1–5] The chemistry is of considerable interest for the potential applications of these materials as catalysts, molecular sieves and as ion exchangers.[6–8] Investigations in this direction have led to many materials of interesting structures, with neutral organic ligands like pyrazine and 4,4′-bipyridine.

Charged ligands like azide and thiocyanate are also used to bridge metal centres, which gives complexes of anomalous architectures with important physical properties such as supramolecular chemistry[9] and molecular magnetism.[10] The thiocyanate and azide[11,12] anions are versatile bridging ligands as they can link a metal centre either end-to-end or end-on, both possibilities being structurally characterized for transition metal complexes.[13,14] When the azido group acts as a bridging ligand with an end-on co-ordination mode the resulting binuclear complexes usually show ferromagnetic behavior, whereas end-to-end co-ordination results in antiferromagnetic behavior.[14]

Interesting studies of μ-thiocyanatocadmium(II) complexes with several kinds of Lewis-base adducts[15–18] and amine ligands[19–24] have been made and the structural varieties have been explained, but μ-azidocadmium(II) complexes are still very few.[25–28]

With various N-substituted ethylenediamines we have been able to obtain some new thiocyanato- and azido-bridged polymeric networks of cadmium(II) with different channel systems. This paper elucidates the synthesis and structural studies of two thiocyanato-bridged and two azido-bridged complexes of cadmium(II). The azido-bridged complexes are the first examples of cadmium(II) chains containing both the bridging modes of azide ligand.

Experimental

Physical measurements and materials

Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 883-IR instrument as KBr pellets. Cadmium(II) acetate dihydrate, sodium thiocyanate, sodium azide (S. D. Fine Chemicals, India), *N*,*N*-diethylethylenediamine (Aldrich) and *N*,*N*-dimethylethylenediamine (Fluka) were of reagent grade and used as received.

Preparations

$[Cd(dmen)(SCN)_2]_n$ 1 and $[Cd(deen)(SCN)_2]_n$ 2. The complexes were prepared by addition of a methanolic solution of dmen (0.11 ml, 1 mmol) for **1** or deen (0.14 ml, 1 mmol) for **2** to a solution of $Cd(OAc)_2 \cdot 2H_2O$ (0.26 g, 1 mmol) in 5 ml methanol at 0 °C with stirring. To the resulting mixture a methanolic solution of NaSCN (0.08 g, 1 mmol) was added very slowly. Shiny colourless crystals appeared within a week, from which those suitable for X-ray analysis were separated and the rest collected by filtration, washed with methanol and dried in air.

$[Cd(dmen)(N_3)_2]_n$ 3 and $[Cd(deen)(N_3)_2]_n$ 4. The complexes were synthesized by mixing a methanolic solution of dmen (0.11 ml, 1 mmol) for **3** or deen (0.14 ml, 1 mmol) for **4** and $Cd(OAc)_2$. $2H_2O$ (0.26 g, 1 mmol) in 5 ml methanol at 0 °C followed by dropwise addition of a concentrated aqueous solution of NaN_3 (0.06 g, 1 mmol). The clear solutions gave transparent crystals after a few days. The analytical results are given in Table 1.

Crystal structure determination

The single crystals of complexes **1**–**4** were mounted on a glass fibre, and placed on a Syntex $P2_1$ 4-circle diffractometer equipped with graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, for the determination of lattice parameters and space group. The crystallographic data are listed in Table 2. The

DOI: 10.1039/b004428h

stability of the crystals was checked by measuring standard reflections at fixed intervals during the data collection. However, no significant losses of intensities were noted. The structures were solved by direct methods using SHELXTL PLUS[29] and refined by a full-matrix least-squares procedure based on F^2 using SHELXL 93.[30]

CCDC reference number 186/2125.

See http://www.rsc.org/suppdata/dt/b0/b004428h/ for crystallographic files in .cif format.

Results and discussion

IR spectra

The complexes **1**–**4** showed several strong bands in the range of 3184 to 3356 cm^{-1}, which can be assigned to the ν(NH) stretching frequency of the NH_2 group. Several bands in the range 2800–3000 cm^{-1} are assigned to aliphatic C–H stretching vibrations. The presence of the bridging thiocyanate groups is indicated by the ν(CN) at 2080, 2106 cm^{-1} for complex **1** and at 2090, 2113 cm^{-1} for **2**. The observed splitting of $\nu_{asym}(N_3)$ stretching into three almost equally intense bands at 2088, 2059 and 2027 cm^{-1} for **3** and at 2092, 2041, 2035 cm^{-1} for **4** indicates the presence of various bridging modes of the azide ligand. All the other bands appeared at their usual positions.

Crystal structures

The labeled structure diagram for complex **1** is shown in Fig. 1 and selected bond distances and bond angles are listed in Table 3. The cadmium atom is in a distorted octahedral environment with the co-ordination of one bidentate amine ligand, two S-bonded thiocyanate ligands and two N-bonded thiocyanate ligands.

The two dimensional polymeric sheet of appreciable thickness about 15.109 Å in the *XY* plane is perpendicular to the *Z* axis (Fig. 2). In the complex each cadmium is linked to four other cadmium atoms through single SCN$^-$ bridges to give 2-D sheet. The NCS–Cd–SCN (92°) linkage is perpendicular to SCN–Cd–NCS linkage, which is more or less *trans* collinear (175°). The rigid rod like nature of the thiocyanate ligand forces the sixteen membered rings to adopt a pseudo chair conformation and fuse to give a honeycomb sheet. The sixteen membered rings are joined to each other in a *cis* fashion along both the axes. The Cd · · · Cd diagonals are 7.13 and 10.44 Å respectively, but near diagonal contacts like S · · · CN of only 4.35 Å are involved.

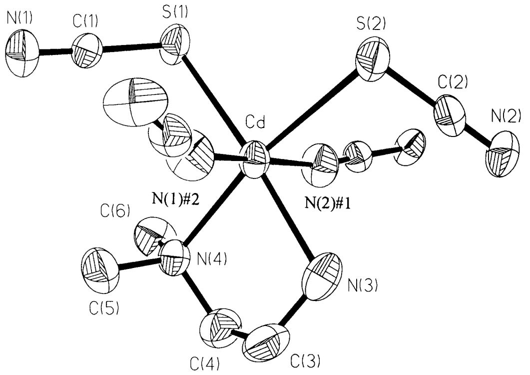

Fig. 1 An ORTEP[31] plot of $[Cd(dmen)(SCN)_2]$ unit of the complex **1** with the atom numbering scheme.

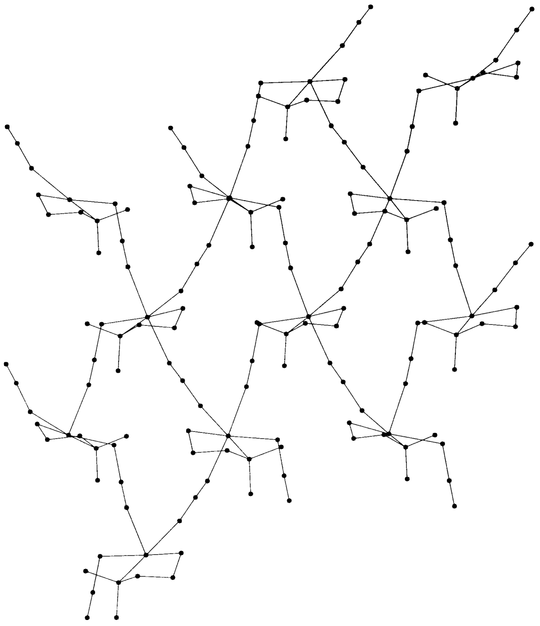

Fig. 2 The polymeric sheet of complex **1** along the *XY* plane.

Table 1 Analytical results

Compound	% found (calc.)			
	C	H	N	Cd
1 $C_6H_{12}CdN_4S_2$	22.5(22.7)	3.9(3.8)	17.7(17.6)	35.0(35.4)
2 $C_8H_{16}CdN_4S_2$	27.3(27.8)	4.8(4.6)	15.9(16.2)	33.0(32.6)
3 $C_4H_{12}CdN_8$	16.9(16.8)	4.1(4.2)	39.2(39.3)	39.0(39.4)
4 $C_6H_{16}CdN_8$	23.2(23.0)	5.1(5.1)	35.7(35.8)	36.1(35.9)

The cadmium co-ordination geometry for complex **2** is similar to that of **1**. The versatile bridging nature of the thiocyanate ligands gives a 1-D polymeric chain, which is presented in Fig. 3 with the atom numbering scheme. Selected bond distances and angles are given in Table 4. In the polymeric chain each cadmium is linked to two other cadmium atoms through paired, nearly linear SCN$^-$ bridges. The C–N–Cd and C–S–Cd linkages are bent and the related bond angles are comparable with those

Table 2 Crystallographic data for complexes **1**, **2**, **3** and **4**

	1	**2**	**3**	**4**
Chemical formula	$C_6H_{12}CdN_4S_2$	$C_8H_{16}CdN_4S_2$	$C_4H_{12}CdN_8$	$C_6H_{16}CdN_8$
Formula weight	316.732	344.654	289.606	312.66
Crystal symmetry	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
a/Å	14.203(10)	13.216(5)	8.926(4)	10.596(7)
b/Å	10.444(7)	9.354(5)	10.836(6)	8.339(4)
c/Å	15.109(12)	10.752(4)	20.827(11)	13.831(9)
β/°		93.01(3)		98.59(5)
V/Å^3	2241(3)	1327.4(10)	2014(2)	2416.8(3)
Z	8	4	8	2
Reflections collected	1030	1326	1119	1159
Independent reflections	1030	1238	1119	1096
*R*1, *wR*2 indices (all data)	0.0198, 0.0453	0.0273, 0.0703	0.0297, 0.0684	0.0237, 0.0432
$I > 2\sigma(I)$	0.0162, 0.0447	0.0256, 0.0698	0.0261, 0.0674	0.0173, 0.0422

Table 3 Selected bond lengths (Å) and bond angles (°) for complex **1**

Cd–N(3)	2.305(3)	Cd–N(2)#1	2.333(4)
Cd–N(4)	2.398(3)	Cd–N(1)#2	2.410(4)
Cd–S(1)	2.630(2)	Cd–S(2)	2.707(2)
N(3)–Cd–N(4)	76.28(12)	N(2)#1–Cd–N(1)#2	175.83(13)
N(3)–Cd–S(1)	170.00(9)	N(4)–Cd–S(2)	170.15(7)
N(4)–Cd–S(1)	95.57(9)	N(3)–Cd–S(2)	94.96(11)
S(1)–Cd–S(2)	92.66(6)	N(3)–Cd–N(2)#1	91.77(13)
N(4)–Cd–N(1)#2	86.96(12)	N(2)#1–Cd–S(1)	94.78(10)
N(1)#2–Cd–S(1)	88.49(9)	N(2)#–Cd–S(2)	89.40(10)

Symmetry transformations used to generate equivalent atoms: #1 $-x + \frac{1}{2}, y + \frac{1}{2}, z$; #2 $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; #3 $-x + \frac{1}{2}, y - \frac{1}{2}, z$; #4 $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 4 Selected bond lengths (Å) and bond angles (°) for complex **2**

Cd(1)–N(1)	2.369(5)	Cd(1)–N(2)	2.349(5)
Cd(1)–N(3)	2.291(4)	Cd(1)–N(4)	2.441(4)
Cd(1)#1–S(1)	2.630(2)	Cd(1)–S(1)#2	2.630(2)
Cd(1)–S(2)#1	2.751(2)		
N(2)–Cd(1)–N(1)	174.38(14)	N(3)–Cd(1)–N(4)	76.54(13)
N(3)–Cd(1)–S(1)#2	178.88(10)	N(2)–Cd(1)–S(1)#2	93.09(10)
N(1)–Cd(1)–S(2)#1	89.69(12)	N(4)–Cd(1)–S(2)#1	161.57(9)
S(1)#2–Cd(1)–S(2)#1	95.15(6)	N(2)–Cd(1)–N(4)	90.65(13)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + \frac{1}{2}, z - \frac{1}{2}$; #2 $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

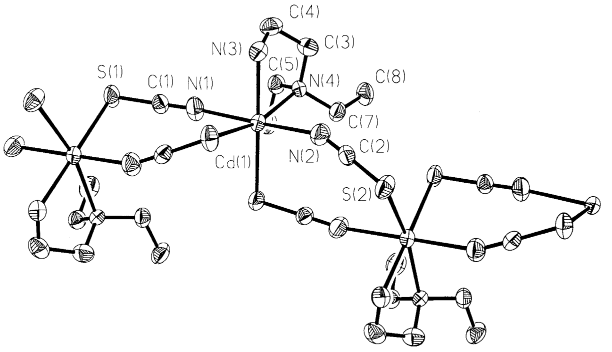

Fig. 3 The molecular geometry and atom numbering scheme of $[Cd(deen)(SCN)_2]_n$ **2**.

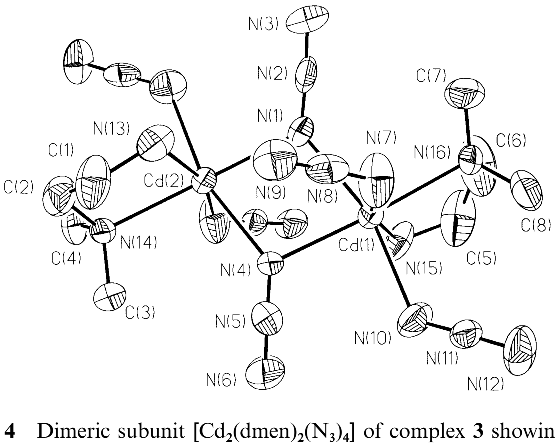

Fig. 4 Dimeric subunit $[Cd_2(dmen)_2(N_3)_4]$ of complex **3** showing the atom numbering scheme.

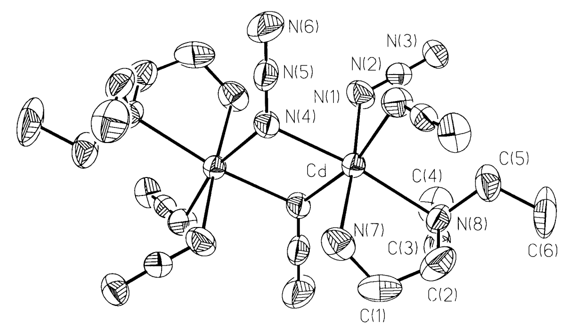

Fig. 5 Dimeric subunit of complex **4** with the atom numbering scheme.

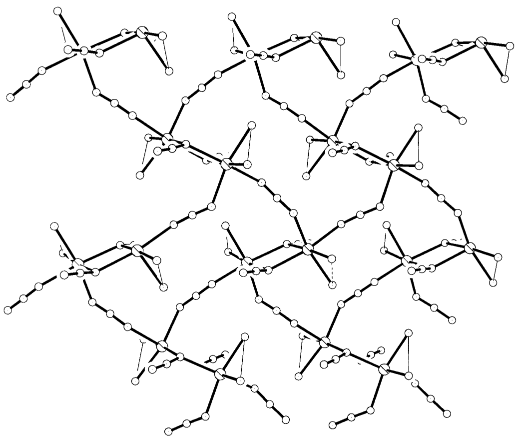

Fig. 6 The 2-D polymeric sheet of complex **3** showing the twenty and four membered rings.

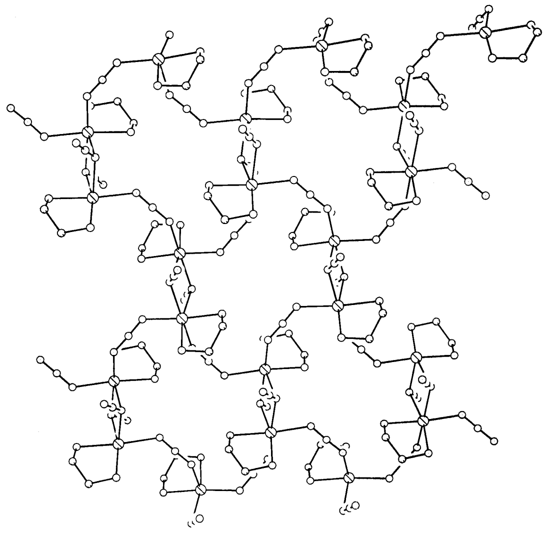

Fig. 7 A view of complex **4** showing the twenty and four membered rings.

of **1** and also in accordance with similar types of reported complexes.[18] The Cd···Cd separation is 8.493 Å.

The non-centrosymmetric unit of complex **3** is shown in Fig. 4 and the centrosymmetric unit of **4** in Fig. 5. Selected bond distances and angles for **3** and **4** are listed in Tables 5 and 6 respectively. Each unit of the complexes consists of a $[Cd(dmen)]^{2+}$ cation with one end-to-end and one end-on bridging azide group. There are two different pseudooctahedrally co-ordinated cadmium centres, with the same environment but different bond parameters for **3**. The deviations of the cadmium atoms from the respective basal planes are 0.011(3) and 0.014(4) Å for compound **3** and 0.145(4) Å for **4**.

The two-dimensional polymeric sheets of complexes **3** and **4** are presented in Figs. 6 and 7 respectively. The double end-on azido bridge forms a dimeric subunit which is further linked to neighbours by a double end-to-end azido bridge. The versatile co-ordination nature of the azide ligand forming the layers results in the formation of a twenty membered zigzag ring, in which a four membered square ring forms a section. For complex **3**, the Cd···Cd separation is 3.63(1) Å for the end-on and

Table 5 Selected bond lengths (Å) and bond angles (°) for complex **3**

Cd(1)–N(7)	2.302(10)	Cd(1)–N(15)	2.313(9)
Cd(1)–N(4)	2.320(9)	Cd(1)–N(1)	2.353(10)
Cd(1)–N(10)	2.380(10)	Cd(1)–N(16)	2.405(9)
Cd(2)–N(12)#1	2.265(11)	Cd(2)–N(1)	2.299(10)
Cd(2)–N(13)	2.315(9)	Cd(2)–N(4)	2.346(9)
Cd(2)–N(9)#2	2.385(11)	Cd(2)–N(14)	2.397(8)

N(7)–Cd(1)–N(15)	161.9(4)	N(7)–Cd(1)–N(4)	96.2(4)
N(15)–Cd(1)–N(4)	100.7(4)	N(7)–Cd(1)–N(1)	92.5(4)
N(15)–Cd(1)–N(1)	97.4(4)	N(4)–Cd(1)–N(1)	77.3(3)
N(7)–Cd(1)–N(10)	89.6(4)	N(15)–Cd(1)–N(10)	85.4(4)
N(4)–Cd(1)–N(10)	85.6(4)	N(1)–Cd(1)–N(10)	162.9(4)
N(7)–Cd(1)–N(16)	86.8(4)	N(15)–Cd(1)–N(16)	76.7(4)
N(4)–Cd(1)–N(16)	175.0(4)	N(1)–Cd(1)–N(16)	98.6(3)
N(12)#1–Cd(2)–N(1)	98.5(4)	N(12)#1–Cd(2)–N(13)	161.1(4)
N(1)–Cd(2)–N(13)	99.7(4)	N(12)#1–Cd(2)–N(4)	89.6(4)
N(1)–Cd(2)–N(4)	77.8(3)	N(13)–Cd(2)–N(4)	99.0(4)
N(12)#1–Cd(2)–N(9)#2	89.2(4)	N(1)–Cd(2)–N(9)#2	86.3(4)
		N(12)#1–Cd(2)–N(14)	85.8(4)
N(13)–Cd(2)–N(9)#2	87.1(3)	N(1)–Cd(2)–N(14)	175.4(4)
N(4)–Cd(2)–N(9)#2	163.7(3)	N(4)–Cd(2)–N(14)	100.7(3)
N(13)–Cd(2)–N(14)	76.1(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; #2 $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; #3 $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; #4 $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 6 Selected bond length (Å) and bond angles (°) for complex **4**

Cd–N(7)	2.305(3)	Cd–N(1)	2.315(4)
Cd–N(4)#1	2.344(4)	Cd–N(4)	2.349(3)
Cd–N(3)#2	2.361(4)	Cd–N(8)	2.418(3)
N(3)–Cd#3	2.361(4)	N(4)–Cd#1	2.344(4)

N(7)–Cd–N(1)	174.52(11)	N(7)–Cd–N(4)#1	88.66(12)
N(1)–Cd–N(4)#1	86.05(13)	N(7)–Cd–N(4)	90.26(13)
N(1)–Cd–N(4)	87.57(13)	N(4)#1–Cd–N(4)	82.02(14)
N(7)–Cd–N(3)#2	97.54(13)	N(1)–Cd–N(3)#2	87.32(14)
N(4)#1–Cd–N(3)#2	166.21(12)	N(4)–Cd–N(3)#2	85.63(13)
N(7)–Cd–N(8)	77.70(12)	N(1)–Cd–N(8)	104.73(13)
N(4)#1–Cd–N(8)	100.86(13)	N(4)–Cd–N(8)	167.49(12)
N(3)#2–Cd–N(8)	92.52(13)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z + 1$; #2 $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; #3 $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

ca. 6.25(2) Å for the end-to-end bridging mode. There are three real Cd···Cd diagonals dividing the rings exactly in two halves, the short diagonal is 6.70(4) Å and two longer ones are 10.40(5) and 11.86(5) Å respectively. The Cd···Cd separations for complex **4** are 3.54(1) and 5.72(1) Å for the end-on and end-to-end bridging respectively. The Cd···Cd diagonal separations are 8.99(5), 9.13(5) and 10.67(5) Å respectively.

Comparing the four structures we have observed the change in dimensions, shape and size with variation of the bidentate amine and bridging ligands. The thiocyanate and azide ligands bridge the cadmium centres in various fashions to give different polymeric constructions. These types of large membered rings with channels are rare. Further investigation, aimed at the production of large membered rings with variable cavities, is in progress.

Acknowledgements

The authors are grateful to the Council of Scientific and Industrial Research and University Grants Commission (New Delhi, India) for financial support.

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