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Crystallochemical formula as a tool for describing metal–ligand complexes – a pyridine-2,6-dicarboxylate example

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Compounds (299) containing 494 symmetrically independent pyridine-2,6-dicarboxylate moieties have been investigated. Among them the structures of $Na_3[Nd(Pydc)_3]\cdot 14H_2O$ and $Na_3[Er(Pydc)_3]\cdot 11.5H_2O$, where H_2Pydc is pyridine-2,6-dicarboxylic acid, were determined by single-crystal X-ray diffraction, while the others were taken from the Cambridge Structural Database. The characteristics of any complex by means of the 'method of crystallochemical analysis' are described, and the coordination types of all the Pydc ions and crystallochemical formulae of all the compounds were determined. Although the ion can act as a mono-, bi-, tri-, tetra- and pentadentate ligand, 96% of Pydc ions are coordinated to the central *A* atom in the tridentate-chelating mode. The dependence of the denticity and geometry of pyridine-2,6-dicarboxylate, as well as of the composition of Pydc-containing complexes, was studied as a function of the nature of the *A* atom, the molar ratio Pydc:*A* and the presence of neutral or acidic ligands in the reaction mixture.

1. Introduction

Pyridinedicarboxylates are of great interest owing to their practical importance, *e.g.* their biological activity (Chung *et al.*, 1971; Lindsay & Murrell, 1986; Hwang *et al.*, 2003), and diverse coordination abilities (Lindsay & Murrell, 1986; Koman *et al.*, 2000; Yue *et al.*, 2005). They can be used to obtain various metal-organic frameworks (Robin & Fromm, 2006), which in some cases exhibit such properties as interesting optical behavior (LeCours *et al.*, 1996; Darling *et al.*, 2000) and magnetism (Brandon, Rittenberg *et al.*, 1998; Brandon, Rogers *et al.*, 1998). The pyridine-2,6-dicarboxylic acid (H_2Pydc) and its alkali salts are most widely used in synthesis. The first X-ray investigation of a Pydc-containing compound was carried out in 1968 and now *ca* 300 structures are available. This allowed us to perform a systematic study of Pydc-containing structures including those of two compounds, $Na_3[Nd(Pydc)_3]\cdot 14H_2O$ (I) and $Na_3[Er(Pydc)_3]\cdot 11.5H_2O$ (II), which we prepared.

The chemical composition of the majority of inorganic and organometallic compounds can be represented by the formula $R_c[A_d \sum_i L_i] \cdot nL_j$, where R is a counter cation; A is the central atom of a complex; L_i are ligands coordinated by the A atom; L_j are counterions or neutral molecules in the outer sphere; c, d and n are the stoichiometric indices. We will focus mainly on $[A_d \sum_i L_i]^{Z\pm}$ complexes. A detailed description of the coordination polyhedron and coordination number (CN) of a central atom reveals the topological role of the metal atom in the structure. At the same time, the coordination types of the L_i ligands and their role are usually only briefly discussed or

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just illustrated by supplementary figures (Robin & Fromm, 2006; Gale & Quesada, 2006).

According to IUPAC recommendations (Connelly *et al.*, 2005), the denticity (*D*) of a ligand is the main descriptor which is equal to the number of ligating atoms attached to the metal atoms. To denote bridging ligands the symbol μ is given as a prefix before the name of the ion or molecule, with a numerical subscript denoting the number of *A* atoms bound to the ligand. The subscript μ does not usually coincide with the denticity of a ligand. For example, in the structures of Tl(HPydc) (WARYEU; Rafizadeh *et al.*, 2005), [Bi(Pydc)Cl(H_2O)] (MIPLUS; Ranjbar *et al.*, 2001) and [Ho(Pydc)(HPydc)] (QUPSUP; Fernandes *et al.*, 2001) the Pydc ions are μ_3 ligands (according to IUPAC recommendations; Connelly *et al.*, 2005), but also tri-, tetra- and pentadentate ones, respectively. From hereon, the Refcode of a compound in the Cambridge Structural Database (CSD; Allen, 2002) is given in parentheses. Thus, the structural role of a ligand in a crystal structure is not clear without establishing the topology of the complex. Recently (Connelly *et al.*, 2005) κ has been used to denote the number and nature of the ligating atoms of a polydentate ligand. Thus, κ^2O in the name of a ligand denotes that it is coordinated by a metal atom (or atoms) through two of its oxygen atoms. The 'kappa nomenclature' has been developed in detail for discrete mono- and polynuclear complexes but even in this case it can be rather bulky. This work presents a method of reproducing the characteristics of any complex by means of the 'method of crystallochemical analysis', which was first suggested by Porai-Koshits & Serezhkin (1994*a*,*b*) and can replace bulky graphical or text descriptions. The principles given below are appropriate for the description of homo- and hetero-, mono- and polynuclear, as well as homo- and heteroligand complexes for which the number of ligating atoms of any ligand varies from one to ten.

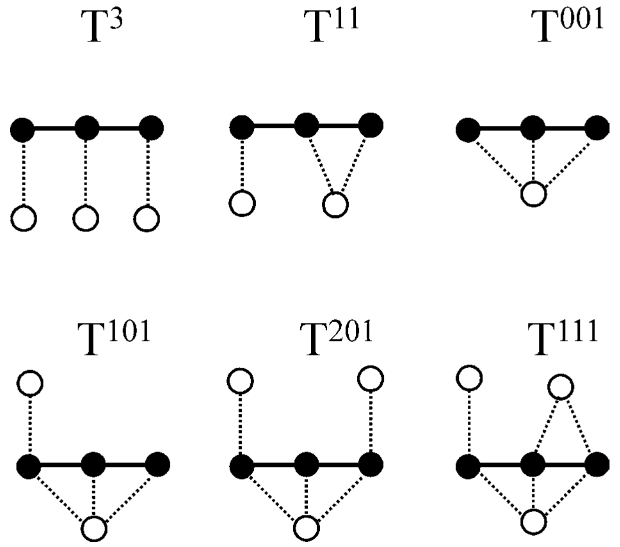

Figure 1
Schematic representation of some coordination types of tridentate ligands. Electron donor atoms are depicted as black circles, metal atoms as empty circles and coordination bonds are shown as dotted lines.

2. Experimental

2.1. Investigation objects

2.1.1. Objects of crystallochemical analysis. The role of pyridine-2,6-dicarboxylate ions in the crystal structures of 299 compounds was studied. Two structures are reported here; information on the crystal structures of the remaining 297 compounds was taken from the CSD provided that:

(i) the central atom of the complex coordinates to at least one pyridine-2,6-dicarboxylate ion,

(ii) the structure refined to $R < 0.1$ and

(iii) there are no disordered non-H atoms.

The alkali ions, organic cations and discrete complex moieties without Pydc ions were considered to be counter ions. Other metal atoms were considered to be complexing ones. The coordination numbers of all the atoms and the crystallochemical formulae of all the complexes were calculated using *TOPOS* (Blatov, 2006).

2.1.2. Synthesis and X-ray investigation of Na_3[Nd(Pydc)$_3$]·14H_2O (I) and Na_3[Er(Pydc)$_3$]·11.5H_2O (II). Bidistilled water was used as a solvent in the synthesis. The reagents $NdCl_3$, $ErCl_3 \cdot 6H_2O$ and H_2Pydc ($C_7H_5NO_4$, pyridine-2,6-dicarboxylic acid) were obtained commercially (Aldrich) and were used without additional purification. In a typical experiment $NdCl_3$ (200 mg, 0.008 mol) or $ErCl_3 \cdot 6H_2O$ (306 mg, 0.008 mol) was dissolved in 20 ml of ambient-temperature water and then a solution of H_2Pydc (401 mg, 0.024 mol) in 20 ml of hot water was added with vigorous stirring. The pH of the reaction mixture was reduced to neutral by the addition of dilute $NaHCO_3$ aqueous solution. The reaction mixture was kept at 333 for 20 min and then left for 12 h at room temperature. Water was removed by a rotary evaporator and the product was washed with cold water to avoid traces of Na_2CO_3 and $NaHCO_3$. The product was re-crystallized from an aqueous ammonia solution (pH $\simeq$ 10); the yield was quantitative.

Single-crystal X-ray diffraction experiments were carried out with a Bruker APEX II CCD at 100 K. The absorption correction was carried out using *SADABS* (Sheldrick, 1998). The structures were solved by direct methods and refined using the full-matrix least-squares technique on F^2 with an anisotropic (for non-H atoms) approximation. H atoms bonded to C were positioned with idealized geometry and fixed C—H distances with U_{iso} values set to $1.2U_{eq}$ of the carrier atom. Water H atoms were found from difference-Fourier maps, normalized to O—H distances of 0.85 Å and refined with fixed O—H distances and U_{iso} values set to $1.5U_{eq}$ of the water oxygen atom. All calculations were performed using *SHELXTL* (Sheldrick, 2008).

2.2. Symbolism of the 'method of crystallochemical analysis' of coordination compounds

2.2.1. Coordination type of a ligand. Let us denote the total denticity of a ligand with *M* for mono-, *B* for bi-, *T* for tri-, *K* for tetra-, *P* for penta-, *G* for hexa-, *H* for hepta-, *O* for octa-, *N* for nona- and *D* for decadenticity. The way in which *A* atoms surround the ligand is denoted by numerical superscripts (*mbtkpghond*). The superscripts define the 'partial' denticity of the ligand with respect to any A atom (m – mono-, b – bi-, t – tri-, …, d – decadenticity). The number of A atoms with respect to the ligand that exhibits the corresponding partial denticity is denoted by the numerical value of the corresponding superscript. Then the coordination type of an ith ligand is given as $D_i^{mbtkpghond}$. A few examples of tridentate ligands coordinated by one, two or three metal atoms are given in Fig. 1, as well as the corresponding coordination-type symbols.

The symbol for the ligand coordination type also denotes the total number of complexing atoms (Z) which surround the ligand, and the total number of chemical bonds that the ligand makes with the central atom (N_B). In the general case for a ligand with a $D_i^{mbtkpghond}$ coordination type

$$Z = m + b + t + k + p + g + h + o + n + d, \quad (1)$$

$$N_B = 1m + 2b + 3t + 4k + 5p + 6g + 7h + 8o + 9n + 10d. \quad (2)$$

For example, for a ligand with T^{001} coordination type $Z = 1$ $(0 + 0 + 1)$ and $N_B = 3$ $(1{\cdot}0 + 2{\cdot}0 + 3{\cdot}1)$, while for that with T^{111} type $Z = 3$ $(1 + 1 + 1)$ and $N_B = 6$ $(1{\cdot}1 + 2{\cdot}1 + 3{\cdot}1)$ (Fig. 1).

2.2.2. Crystallochemical formula of a complex. Provided that the coordination types of all the ligands in a complex are determined, the crystallochemical formula (CCF) of the complex can be written. Any CCF includes the coordination types of all the ligands with the same chemical formula (with the exception of counterions and molecules). The subscripts denote the stoichiometric composition with respect to any equivalent ligand and A atom. For example, the $[Nd(Pydc)_3]^{3-}$ complex in the structure of (I) is characterized by AT_3^{001} CCF (Fig. 2).

A superscript after the A symbol represents the number of metal–metal bonds in the complex that the complexing atom is involved in. For instance, the Re complex in $[Re_2(Pydc)((PPh_2)CH_2(PPh_2))_2Cl_2]{\cdot}C_6H_6$ (IQAMUI; Chattopadhyay *et al.*, 2003) is given as $A_2^1T^{001}B_2^2M_2^1$ CCF (Fig. 2). If two chemically nonequivalent complexing atoms or ligands are present in a complex, A and A', M^1 and M'^1 *etc.* symbols should be used. For example, the copper complex in $[Cu(Pydc)(Pyca)]{\cdot}2H_2O$ (Pyca = pyridine-2,6-dicarboxamide, FEKYIE; Brandi-Blanco *et al.*, 2005) has $AT^{001}T'^{001} = AT_2^{001}$ CCF (Fig. 2). If there are two different complexes in a structure, the plus sign should separate their CCFs, as in AM_6^1 + $A'T_3^{001}$ CCF for $[Co(NH_3)_6][La(Pydc)_3]{\cdot}5H_2O$ (NALBAE; Brayshaw *et al.*, 2005), where A = Co, A' = La. Sometimes the same ligands being in the same complex differ in coordination types, as in the case of $[Sr_2Ce_2(Pydc)_6(H_2O)_{10}]{\cdot}6H_2O$ (YAZYAA; Prasad & Rajasekharan, 2005) with $A'_2A_2K_3^{101}T_3^{001}M_{10}^1 = A'_2AK_3^{101}M_{10}^1 + AT_3^{001}$ CCF.

2.2.3. How to calculate the descriptors of the coordination sphere of atom *A*. Using the chemical and crystallochemical formulae of a complex together allows the environment of the central atom to be characterized in order to calculate the coordination number (CN) and the number of ligands in the first coordination sphere (N_A) without any diagramatical or text description. Besides, if a complex contains bridging ligands, the descriptors of the second coordination sphere also become of interest, *e.g.* in theory, the maximum number of A atoms that surround the central ones and are connected to them through the bridging ligands (C_T). In the general case $CN(A)$, N_A and C_T can be expressed as

$$CN(A) = a + \sum_i \nu_i(m + 2b + 3t + 4k + 5p + 6g + 7h + 8o + 9n + 10d)_i, \quad (3)$$

$$N_A = a + \sum_i \nu_i(m + b + t + k + p + g + h + o + n + d)_i, \quad (4)$$

$$C_T = a + \sum_i \nu_i(m + b + t + k + p + g + h + o + n + d)_i \times (m + b + t + k + p + g + h + o + n + d - 1)_i, \quad (5)$$

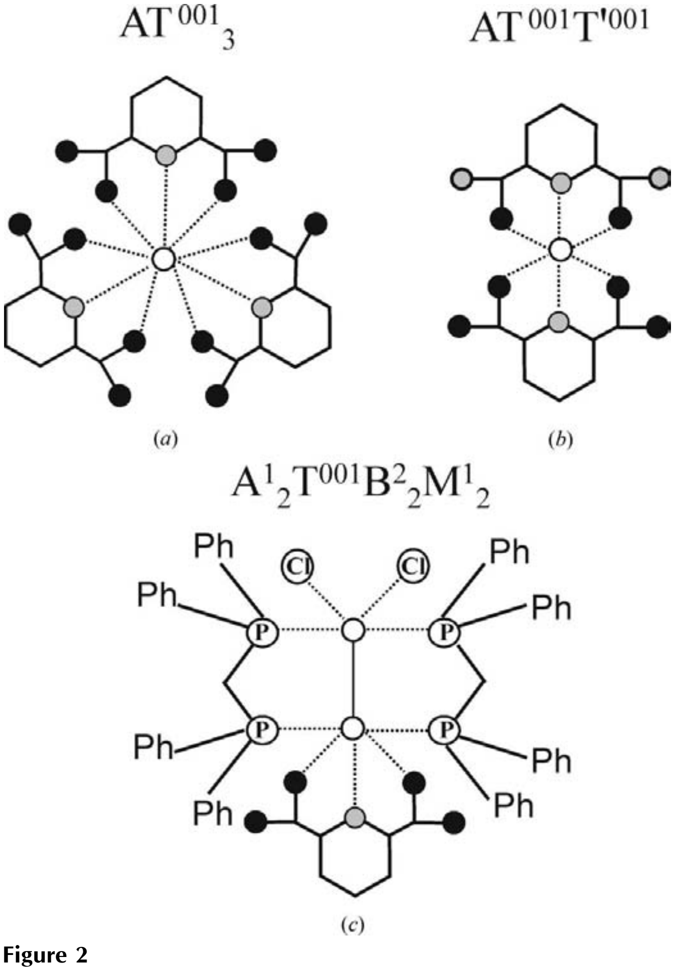

Figure 2
Schematic representation and CCF of (*a*) neodymium, (*b*) copper and (*c*) rhenium (bottom) complexes in the structures of $Na_3[Nd(Pydc)_3]{\cdot}14H_2O$ (I), $[Cu(Pydc)(Pyca)]{\cdot}2H_2O$ (FEKYIE; Brandi-Blanco *et al.*, 2005) and $[Re_2(Pydc)((PPh_2)CH_2(PPh_2))_2Cl_2]{\cdot}C_6H_6$ (IQAMUI; Chattopadhyay *et al.*, 2003). Metal atoms are depicted as empty circles, coordination bonds are shown as dotted lines, O atoms are depicted as black circles, N atoms – as grey circles, and P and Cl atoms are labeled.

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{21}H_{25}N_3Na_3NdO_{20}\cdot 6H_2O$	$C_{21}H_{25}ErN_3Na_3O_{20}\cdot 3.5H_2O$
M_r	960.75	938.73
Cell setting, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	100 (2)	100 (2)
a, b, c (Å)	10.2800 (5), 10.9960 (5), 17.1772 (8)	9.6488 (8), 18.9547 (15), 17.8915 (14)
α, β, γ (°)	73.7610 (10), 77.5970 (9), 72.8990 (10)	90.00, 91.7350 (10), 90.00
V (Å^3)	1763.12 (14)	3270.7 (5)
Z	2	4
D_x (Mg m^{-3})	1.810	1.906
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.61	2.71
Crystal form, color	Prism, pink	Cube, pink
Crystal size (mm)	0.41 × 0.35 × 0.21	0.26 × 0.26 × 0.22
Data collection		
Diffractometer	Bruker SMART APEX II CCD area detector	Bruker Apex II CCD area detector
Data collection method	ω scans	ω scans
Absorption correction	Multi-scan†	Multi-scan†
$T_{\min}$	0.520	0.500
$T_{\max}$	0.710	0.561
No. of measured, independent and observed reflections	27 023, 12 686, 11 641	35 493, 8629, 6822
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.028	0.051
$\theta_{\max}$ (°)	32.5	29.0
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.068, 1.01	0.062, 0.185, 1.02
No. of reflections	12 686	8629
No. of parameters	490	443
H-atom treatment	Constrained‡	Constrained‡
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 1.2P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.120P)^2 + 11.P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.004	0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.52, −1.13	3.32, −3.91

Computer programs used: *APEX*2 (Bruker, 2005), *SHELXTL* (Sheldrick, 2008). † Based on symmetry-related measurements. ‡ Constrained to parent site.

where a is the number of metal–metal bonds; $m, b, t \ldots d$ are the number of A atoms, coordinating the ligand through one, two, three ... ten bonds; and ν_i is the stoichiometric coefficient which indicates the number of ligands of type i in the CCF.

The real number of A atoms that surround the central ones through the bridging ligands (C_P) is less than or equal to C_T because some bridging ligands can chelate A atoms, which is why the C_P value cannot be calculated from the CCF except in obvious cases where $C_T = 0$ or 1. Thus, C_T is an independent descriptor that characterizes the topology of a complex. Finally, we should mention the dimensionality of complex groups which are able to form discrete groups, chains, layers or frameworks.

For example, in $[Sn(Pydc)(CH_3)_2]$ (MAZREL; Ma *et al.*, 2005; Fig. 3*a*) with $AK^{011}M_2^1$ CCF, $CN(Sn) = 1\cdot(1\cdot0 + 2\cdot1 + 3\cdot1) + 2\cdot(1\cdot1) = 7$, $N_A = 1\cdot(0 + 1 + 1) + 2\cdot(1) = 4$ and $C_T = 1\cdot(1 + 1)\cdot(1 + 1 - 1) + 2\cdot1\cdot(1 - 1) = 2$. Here $C_P = C_T = 2$ and the complex is a discrete trinuclear one. At the same time for $C_p = 2$ an isomeric complex is possible with the same CCF and topological descriptors, but with chain structure (Fig. 3*b*). Hence, the full topological description of the complex includes the CCF, C_P and the dimensionality of the complex.

3. Results and discussion

3.1. Crystal structure of $Na_3[Nd(Pydc)_3]\cdot 14H_2O$ and $Na_3[Er(Pydc)_3]\cdot 11.5H_2O$

The main structural units of (I) and (II) are discrete mononuclear groups with the composition $[Ln(Pydc)_3]^{3-}$ (Ln = Nd and Er; the *ORTEP* view of the former is given in Fig. 4). The Pydc anions for all cases are tridentate-chelating and both complexes belong to AT_3^{001} CCF. The CN(Ln) = 9, LnO_6N_3 (Ln = lanthanide) coordination polyhedron is a tricapped trigonal prism, with O atoms in the base of the prism. The molecular view of $[Ln(Pydc)_3]^{3-}$ anions, *ORTEP* view of unit cells, crystal packing and hydrogen-bond tables for both complexes are given as supplementary material.[1] Experimental details are summarized in Table 1.

Complex (I) contains four crystallographically independent Na ions, two of them (Na1 and Na2) are located in special positions. The coordination polyhedra of Na1, Na2 and Na3 are square bipyramids with carboxylic O atoms in axial positions and water molecules in equatorial ones; Na4 coordinates three carboxylic and three water oxygen atoms. Each Na is connected to two Pydc anions that belong to different discrete complex groups, and all three ligands in the $[Nd(Pydc)_3]^{3-}$ complex are connected with Na, to form a framework of composition $[Na_3Nd(Pydc)_3(H_2O)_8]$. Six more water molecules occupy the framework voids and are involved in hydrogen bonding. The Na3 ion in the structure of (II) is disordered over two positions with 0.75 and 0.25 occupancies. Cheng *et al.* (2004) have recently reported the structure of $Na_3[Er(Pydc)_3]\cdot 11.5H_2O$ (LAHPEQ) studied at room temperature. The authors found all non-H atoms to be ordered, but did not locate H atoms on solvent water molecules. We reinvestigated (II) as an example of a lanthanide-containing compound and to clarify if the hydrogen-bond

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: GP5026). Services for accessing these data are described at the back of the journal.

system influences the planarity and arrangement of Pydc ions. Two Na ions in the structure of (II) have $CN = 6$ and a square-pyramidal coordination polyhedron with O atoms of the carboxylic groups in axial positions, and those of water molecules in equatorial positions. The remaining disordered Na ion (as well as the corresponding ordered Na atom in LAHPEQ) has $CN = 5$. Its coordination polyhedron is a square pyramid with one O atom of the carboxylic group in the base of the pyramid and those of water molecules in other pyramid vertexes. Only two of the $[\mathrm{Er(Pydc)_3}]^{3-}$ ligands are also coordinated with Na, so in the structure of (II) chains of the composition $[\mathrm{Na_3Er(Pydc)_3(H_2O)_8}]$ were found to be parallel to the crystallographic *a* axis (see supplementary material). The chains and remaining water molecules are linked into a framework through hydrogen bonds.

Taking into account the number and site symmetry of Na ions and water molecules coordinated by Na ions (some are bridges between Na ions), the CCFs of $[\mathrm{Na_3Nd(Pydc)_3(H_2O)_8}]$ and $[\mathrm{Na_3Er(Pydc)_3(H_2O)_8}]$ moieties become $A'_3AP^{301}P_2^{201}M_3^2M_5^1$ and $A'_3AP^{401}K^{101}T^{001}M_4^2M_4^1$, respectively (where A' = Na, A = Ln). Both CCFs are given in the short form that does not show the coordination number of each atom. The expanded CCFs represent the partial denticities of each ligand with respect to each type of A atom given as subscripts and reproduce the coordination environment and coordination number of all metal atoms of the complex. In the structures of (I) and (II) the expanded CCFs are, respectively, $A'_3AP^{301}P_2^{201}M_3^2M_5^1 = AP_{001/301}P_{002/201} \times A'P_{200/201}M_{2/2}M_{2/1} \times A'P_{100/301}P_{100/201}M_{3/2}M_{1/1} \times A'P_{200/301}P_{100/201}M_{1/2}M_{2/1}$ and $A'_3AP^{401}K^{101}T^{001}M^2{}_4M^1{}_4 = AP_{001/401}K_{001/101}T_{001/001} \times A'P_{200/401}M_{4/2} \times A'P_{100/401}K_{100/101}M_{3/2}M_{1/1} \times A'P_{100/401}M_{1/2}M_{3/1}$.

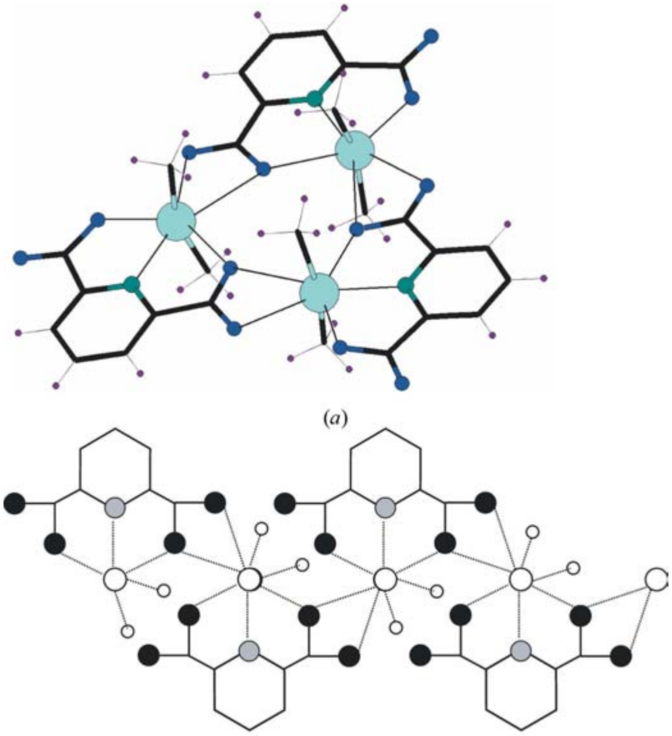


Figure 3
(*a*) Molecular and (*b*) schematic view of complexes with $AK^{011}M_2^1$ CCF given for the discrete trinuclear group in the structure of $[\mathrm{Sn(pydc)(CH_3)_2}]$ (MAZREL; Ma *et al.*, 2005), and possible chain group, respectively.

3.2. Coordination types of pyridine-2,6-dicarboxylate anions

There are 494 symmetrically independent Pydc ions which are found in the structures of 299 compounds that form 19 coordination types (Fig. 5). Among these types three pairs in fact belong to the same coordination type. Two pairs differ in the nature of the ligating atoms: B^{01}-κ^2N,O and B^{01}-κ^2O or T^{11}-κ^3N,O,O' and T^{11}-κ^3O,O,O' (the type of ligating atom is given in terms of kappa nomenclature; Connelly *et al.*, 2005). The third (K^{201}-*cis* and K^{201}-*trans*) pair differs in the monodentate bonding character with two metal atoms ($m = 2$): to the same (*cis*) or different (*trans*) carboxylic groups of the Pydc ion. Pydc ions are coordinated by the metal atom through one (always the O atom), two, three, four or five donor atoms, being, respectively, mono-, bi-, tri-, tetra- or pentadentate ligands (Fig. 5). Since both N and O atoms of pyridinedicarboxylates can coordinate the metal atom, the nature of the donor atoms is obvious only in the case of the pentadentate ligand. For the other cases, atoms (O or N) involved in bonding should be highlighted. However, these would make the crystallochemical formula bulky and difficult to identify. This is the reason why the nature and the number of donor atoms are given below only for B^{01} and T^{11} coordination types. For the other cases this information can be obtained from Fig. 5.

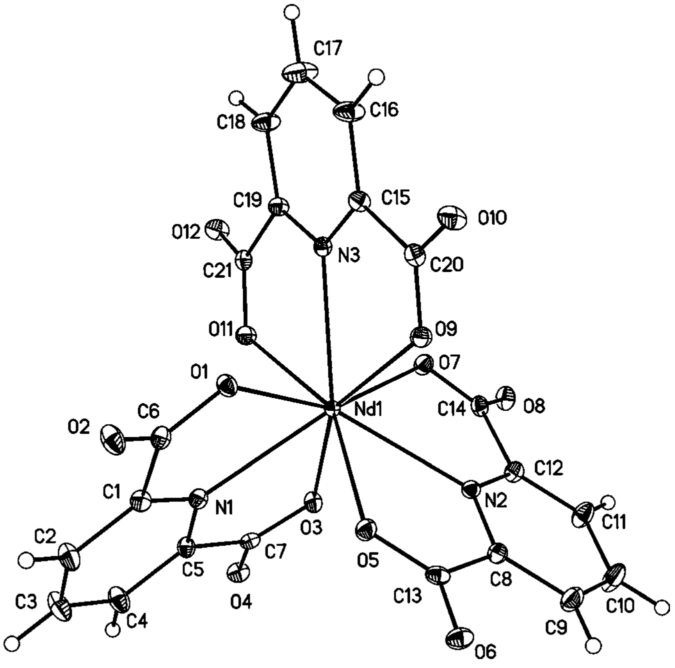


Figure 4
ORTEP view (given with 50% probability level) of $[\mathrm{Nd(Pydc)_3}]^{3-}$ in the structure of (I).

Table 2
Dependence of φ dihedral angles on the coordination type of the Pydc ion.

Pydc coordination type	No. of Pydc ions	Ratio (%)	φ (°)
T^{001}	356	72.1	7 (5)
K^{101}	58	11.7	11 (5)
T^{101}	25	5.1	8 (4)
P^{201}	17	3.5	13 (6)
K^{201}-*trans*	8	1.6	10 (4)
B^{01}-κ^2N,O	6	1.2	39 (16)
T^{201}	4	0.8	11 (7)
B^2	3	0.6	8 (3)
K^{011}	3	0.6	7 (7)
K^{201}-*cis*	3	0.6	9 (4)
M^1	2	0.4	10 (5)
T^{11}-κ^3N,O,O'	2	0.4	31 (13)
B^{01}-κ^2O	1	0.2	14
T^{11}-κ^3O,O,O'	1	0.2	16
T^{21}	1	0.2	16
K^{02}	1	0.2	3
P^{021}	1	0.2	8
P^{111}	1	0.2	9
P^{211}	1	0.2	17
Total	494	100	9 (6)

It was found that the Pydc ion in crystal structures can make from 1 to 7 bonds with *A* atoms (Fig. 5), so the number of *A* atoms coordinating the ion varies from 1 to 4. According to data obtained (Table 2) the tridentate-chelate coordination type T^{001} of Pydc ions is the most frequent (72% of compounds). In this case the metal atom forms two five-membered metallocycles at the same time. Moreover, 96% of compounds contain Pydc ions for which $t = 1$ (T^{001}, T^{101}, T^{201}, K^{011}, K^{101}, K^{201}, P^{021}, P^{111}, P^{201} and P^{211}). In other words, in the vast majority of cases the Pydc anion is the tridentate-chelating ion with respect to one *A* atom (Table 2). Interrelations between some coordination types of Pydc ion and the nature of the *A* atom, the Pydc:*A* molar ratio, and the presence of other acidic or neutral ligands are discussed in §3.3.

Let us stress that the name of the compound in IUPAC terms can be derived easily if the chemical and crystallochemical formulae of the complex are found, but not *vice versa*. This point can be illustrated by using the aforementioned Tl(HPydc) (WARYEU; Rafizadeh *et al.*, 2005), [Bi(Pydc)Cl(H_2O)] (MIPLUS; Ranjbar *et al.*, 2001) and [Ho(Pydc)(HPydc)] (QUPSUP; Fernandes *et al.*, 2001) compounds. The complexes have the following CCFs: AT^{201}, $AK^{201}M^1M'^1$ and $AP^{201}T^{001}$, respectively, and include tri-, tetra- and pentadentate Pydc ions (Fig. 6). In all cases three metal atoms coordinate the Pydc ligand [$m + b + t = 2 + 0 + 1$, see equation (1)], *e.g.* according to IUPAC recommendations (Connelly *et al.*, 2005) the Pydc ions are μ_3 ligands. To derive μ_i from the coordination type of a ligand one can use the graphical procedure of ligand contraction to a point (Fig. 6, right column). In fact, the IUPAC name of a compound includes information on the number of metal atoms bound to a ligand, but has no information about the real number of metal–ligand bonds. Thus, sometimes it is impossible to determine, for example, the coordination number of an atom using only the IUPAC name of a compound.

3.3. Peculiarities of the Pydc anion geometry

Chemical bonds between heterocyclic and carboxylic groups of the Pydc ion are standard [average r(C—C) bond length = 1.51 (2) Å], but the ion is planar in most cases. As a result, the dihedral angle (φ) between the mean planes of the carboxylic groups is close to 0°. Thus, for all 494 Pydc ions under discussion the average φ value is $9 \pm 6°$ (Table 2), while in the structures of 11 organic compounds containing isolated pyridine-2,6-dicarboxylic acid moieties the average φ value is $5 \pm 2°$. At the same time there are 153 and 5 Pydc ions with φ in the ranges $10 \le \varphi \le 30$ and $30 < \varphi \le 62°$, respectively. The dependence of the average φ value on the coordination type of Pydc ion is given in Table 2. It was found that the Pydc ions involved in the formation of two five-membered metallocycles with the *A* atom ($t = 1$) are planar within $3\sigma(\varphi)$. According to our data, in contrast to the oxalate-containing compounds (Serezhkin *et al.*, 2005), the nature and number of counterions, as well as the presence of hydrogen bonds do not influence the planarity and arrangement of the Pydc ions.

All compounds containing B^{01}-κ^2N,O or T^{11}-κ^3N,O,O' Pydc ions (and have maximal φ values) are listed in Table 3. It seems that both a high φ value and the appearance of these rare coordination types are caused by the nature of the central atom and steric hindrance. For example, for Pt and Pd square complexes with AB^{01}_2 CCF both ligands lie on one plane. Thus,

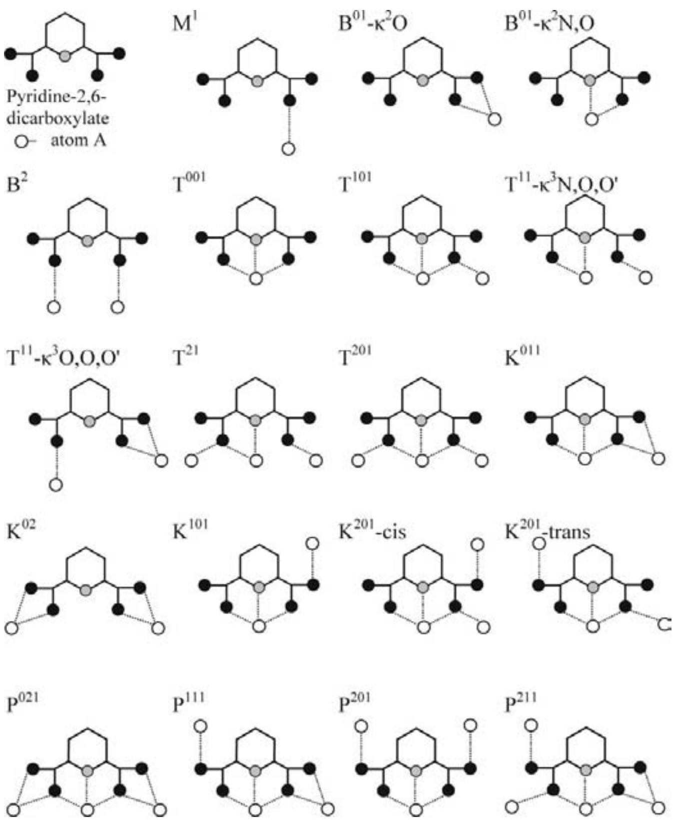


Figure 5
Types of pyridine-2,6-dicarboxylate ion coordination.

Table 3
Complexes with B^{01}-κ^2N,O or T^{11}-κ^3N,O,O' coordination types of Pydc ions.

Compound	Crystallochemical formula	*CN*(*A*)	φ (°)	Refcode
$NH_4[Ru(Pydc)_2Cl_2]$	$AB^{01}_2M^1_2$	6	62	DAZZOT
$Na_2[Pt(Pydc)_2]\cdot6H_2O$	AB^{01}_2	4	46	JILDIR
$Na_2[Pt(Pydc)_2]\cdot6H_2O$	AB^{01}_2	4	46	JILDIR01
$[Pd(Pydc)(C_{12}N_2H_8)]\cdot4H_2O$	AB^{01}_2	4	36	CAQTEU
$[Zn(HPydc)_2(H_2O)]\cdot3H_2O$	$AT^{001}B^{01}M^1$	6	26	HECMEI
$[Fe(HPydc)_2(H_2O)]\cdot3H_2O$	$AT^{001}B^{01}M^1$	6	19	ZILZUP
$\{Pd(Pydc)[P(C_4H_9)_3]\}_2$	$AT^{11}M^1$	4	43	ZUVQAI
$[Re_2(Pydc)(P_2C_{25}H_{12})_2Cl_2]\cdot2CH_2Cl_2$	$A^1_2T^{11}B^2_2M^1_2$	5, 6	21	ULEXOY

Table 4
Crystallochemical formulae of lanthanide complexes containing Pydc ions.

Pydc:*A* ratio	Complex	*A*†	*CN*(*A*)†	Crystallochemical formula	Complex dimensionality
3	$[Ln(Pydc)_3]^{3-}$	La–Er, Yb, Lu	9	AT^{001}_3	Discrete mononuclear
2	$[Ln(Pydc)_2]^-$	Ho	8	$AP^{201}T^{001}$	Layer
	$[Ln(Pydc)(HPydc)(H_2O)_2]$	La–Eu	9	$AK^{101}T^{001}M^1_2$	Chain
	$[Ln(Pydc)_2(H_2O)_2]^-$	La, Ce	9	$AT^{101}T^{001}M^1_2$	Discrete binuclear
	$[Ce(Pydc)_2(H_2O)_3]$	Ce	9	$AT^{001}_2M^1_3$	Discrete mononuclear
	$[Ln(Pydc)_2(H_2O)_3]^-$	Sm, Gd			
1.67	$[Ln_3(Pydc)_5(H_2O)_8]^-$	2La + Eu, Pr	9	$A_3P^{201}K^{101}_2T^{001}_2M^1_8$	Layer
	$[Ce_3(Pydc)_3(HPydc)_2(H_2O)_2]^+$	Ce	9, 8	$A_3P^{201}_3K^{101}_2M^1_2$	Framework
1.50	$[La_2(Pydc)_3(H_2O)_3]$	La	8	$A_2K^{101}K^{011}T^{101}M^1_3$	Chain
	$[Ln_2(Pydc)_3(H_2O)_3]$	La–Pr, Sm	9, 8	$A_2P^{201}K^{201}K^{101}M^1_3$	Framework
	$[Sr_2Ce_2(Pydc)_6(H_2O)_{10}]$	(Sr) Ce	(8), 9	$A'_2A_2K^{101}_6M^1_{10}$	Discrete tetranuclear
1.33	$[Cu_2Ln(Pydc)_3(HPydc)H_2O)_2]$	(Cu) La, Pr	(6), 6	$A'_2AK^{101}_4M^1_2$	Chain
1.20	$[Mn_3Ln_2(Pydc)_6(H_2O)_6]$	(Mn) Er, Gd	(6), 9	$A'_3A_2P^{201}_6M^1_6$	Framework
1	$[Pr_2(Pydc)_2(SO_4)(H_2O)_5]$	Pr	10, 9	$A_2P^{111}T^{101}K^{02}M^1_5$	Layer
	$[La_4(Pydc)_4(Mo_8O_{26})(H_2O)_4]$	La	8, 6	$A_4P^{201}_2K^{201}_2K^4M^1_4$	Framework

† Atoms (and corresponding coordination numbers) of complementary (with respect to the Ln atom) complexing atoms are given in parentheses.

the planar geometry of the Pydc ion (with $\varphi = 0$) would result in O···O (*A* = Pt) or O···H (*A* = Pd) distances between two carboxylic groups, or a carboxylic group and a 1,10-phenanthroline group which are too short. In the case of octahedral complexes of Ru ($AB^{01}_2M^1_2$), Fe and Zn ($AT^{001}B^{01}M^1$) the repulsion between carboxylic group and monodentate ligand also leads to high φ-angle values. Two more compounds have bridging non-planar Pydc ions in their structures because of the repulsion of the carboxylic group from bulky ^{n}Bu$_3$P groups (*A* = Pd) or coordination to the Re_2 cluster.

3.4. What defines the geometry and composition of Pydc-containing complexes?

It was stated that the reduction of the anion is accompanied by a decrease in the number of ligating atoms of the Pydc group. Only the $Pydc^{2-}$ anion can be a pentadentate ligand, whilst $HPydc^-$ denticity does not exceed three.

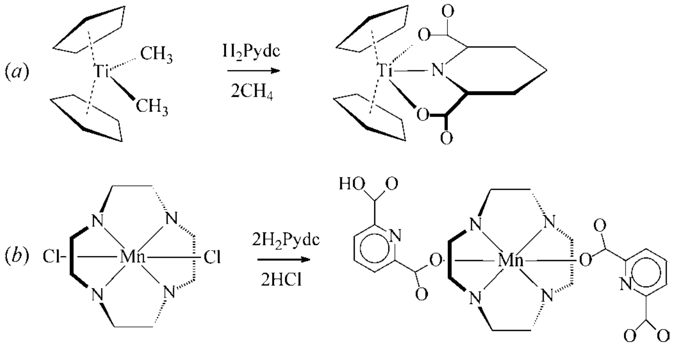
3.4.1. Nature of the *A* atoms and molar ratio Pydc:*A*. For 299 compounds the most frequent crystallochemical group is AT^{001}_2, which corresponds to the bis(pyridine-2,6-dicarboxylates) of Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pt and Zn. This group includes 51 complexes of mono-, bi- or trivalent metals with $Pydc^{2-}$ or $Hpydc^-$. All *A* atoms have *CN*(*A*) = 6 and an octahedral coordination polyhedron, formed by two perpendicular anions. Here *A* atoms are *d*-block elements, thus the aforesaid CN and coordination polyhedron are widespread among them. This fact together with the greater electron-donor ability of the anion with respect to the neutral water molecule seem to be the reasons for the prevalence of the side bis(pyridinedicarboxylates).

Complexes which contain more than two Pydc anions in the coordination sphere of the central atom start to appear for the 4*d*-block elements; such complexes are most frequent for lanthanides (Ln, see below). For other *p*- and *d*-block elements the increase in ionic radius and the maximal coordination number of an element is accompanied either by the coordination of other ligands present in the reaction mixture (*e.g.* solvate molecules) or an increase in the number of Pydc ligating atoms. Thus, among complexes with Pydc:*A* = 2 and *A* = Ga, In, those with compositions $[Ga(Pydc)_2]^-$ and $[In(Pydc)_2(H_2O)_2]^-$ (their CCFs are AT^{001}_2 and $AT^{001}_2M^1_2$), in which the increase in number of solvate molecules is obvious, can be observed. The coordination type T^{001} (*Z* = 1) is then realised in the structures of compounds with *A* = Ga, In, Sn and Sb, whilst T^{101}, K^{201} and P^{211} coordination types (*Z* = 2, 3 and 4, respectively) were found in complexes of Tl^{I}, Pb^{II} and Bi^{III}.

The molar ratio Pydc:*A* in lanthanide compounds varies from 1 to 3 (other complexing atoms are also taken into account, Table 4). Since lanthanides have high coordination numbers, the smaller the Pydc:Ln ratio the higher the number of Ln atoms bound with one anion. For example, the coordination type T^{001} was found in complexes with Pydc:Ln $\geq$ 1.67, while only tetra- and pentadentate ligands were present for Pydc:Ln $\leq$ 1.50. Thus, in the vast majority of cases even for the ratio Pydc:Ln < 3 an Ln atom coordinates at least two Pydc anions. As a result, the decrease in the Pydc:Ln ratio is accompanied by a change from discrete to layer and framework $[Ln_a(Pydc)_b]$ complexes.

To summarize, with excess Pydc anions in the reaction mixture, 3*d* and Ln atoms will preferentially form bis(pyridine-2,6-dicarboxylato) and tris(pyridine-2,6-dicarboxylato)anions, respectively. The elements situated in between in the periodic table readily form heteroligand (*e.g.* oxo, hydroxo and solvate) complexes with Pydc:*A* $\leq$ 2. The inert 6*s* electron pair prevents 6*p* elements from forming tris(pyridine-2,6-dicarboxylates). Nevertheless, complexes of all elements of the sixth-period with tetra- and pentadentate Pydc anions are quite widespread. Besides, the increase in ligand denticity may be conditioned by a decrease in the Pydc:*A* molar ratio of the complex (and in the reaction mixture).

3.4.2. Mixed-ligand complexes and conditions of synthesis. A number of mixed-ligand complexes contain other neutral or acidic ligands (mono-, bi-, tri-, tetra- or pentadentate) in addition to Pydc. Complexes containing water, oxo or hydroxyl groups, halogenides and alcohols are widespread among monodentate ones. 53 compounds include bridging or terminal bidentate ligands. Four complexes exist with tridentate ligands which are 2,6-substituted pyridine derivatives with donor O or N atoms. The pentadentate ligands (except Pydc) were found in the structures of $[Ti(Cp)_2(Pydc)]$ (FEKHIM; Leik *et al.*, 1986) and $[Zr(MeCp)_2(Pydc)]$ (HAMSIX; Niemann *et al.*, 1993). The tetradentate ligands are sulfate, 1,4,8,11-tetraazocyclodecan (tacd) and its 2,5,9,12-tetramethyl derivative which are found in the structures of $[Pr_2(Pydc)_2(SO_4)(H_2O)_5]\cdot 2H_2O$ (FIPPOK; Zhao *et al.*, 2005), $[Mn(tacd)(Pydc)(HPydc)]\cdot 2H_2O$ (AQAWEU; Shaikh *et al.*, 2004) and $[Ni(Me_4tacd)(Pydc)]\cdot 2H_2O$ (XUYHEE; Choi *et al.*, 2003). We shall discuss the importance of conditions of synthesis using examples of complexes with tetra- and pentadentate ligands. The Pydc-containing compounds with Cp, tacd and Me_4tacd were obtained by the reaction of H_2Pydc (or pyridine-2,6-dicarboxylate alkali salt) and Cp metal complexes (*a* in the scheme) or tacd (*b* in the scheme) derivatives, namely, $[Ti(Cp)_2(CH_3)_2]$, $[Mn(tacd)Cl_2]Cl\cdot H_2O$ and $[Ni(tacd)(H_2O)_2]Cl_2$. Usually pyridine-2,6-dicarboxylate is not able to replace a π or complex chelate ligand in the coordination sphere of a metal, only easy leaving groups.



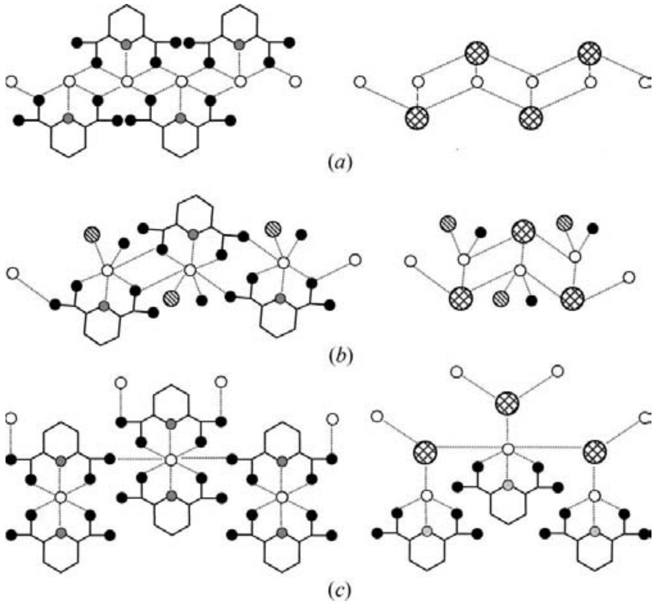


Figure 6
Schematic representation of complex ions in the structures of (*a*) Tl(HPydc) (WARYEU; Rafizadeh *et al.*, 2005), (*b*) $[Bi(Pydc)Cl(H_2O)]$ (MIPLUS; Ranjbar *et al.*, 2001) and (*c*) [Ho(Pydc)(HPydc)] (QUPSUP; Fernandes *et al.*, 2001). The right column represents pyridine-2,6-dicarboxylate ions with μ_3 coordination (in accordance with IUPAC rules) as full circles.

Since in the structures of the initial $[Mn(tacd)Cl_2]^-$ and $[Ni(tacd)(H_2O)_2]^{2-}$ complexes the monodentate terminal groups are in the axial positions of the MnN_4Cl_2 and NiN_4O_2 octahedra, it is not surprising that their substitution by Pydc leads to the formation of rare M^1 and B^2 coordination types. At the same time, the $[Pr_2(Pydc)_2(SO_4)(H_2O)_5]\cdot 2H_2O$ (FIPPOK; Zhao *et al.*, 2005) complex was obtained by hydrothermal synthesis from H_2Pydc, Pr_6O_{11} and $(NH_4)_2SO_4$. In its structure both the Pydc and sulfate anions form standard (for them) coordination types: P^{111} or T^{101} for the former and K^{02} for the latter. Hence, information on the structure (and, consequently, about CCF) of the initial complex and the synthesis conditions suggests the composition and structure of the intermediate and final complexes.

4. Conclusions

Crystallochemical analysis of 299 compounds containing 494 symmetrically independent pyridine-2,6-dicarboxylate moieties in their structures was carried out. The coordination of the pyridine-2,6-dicarboxylate to a metal atom in a tridentate-chelating mode forming two five-membered metallocycles was found to be characteristic for this anion. The 3*d* elements and lanthanides usually form bis- and tris(pyridine-2,6-dicarboxylates), respectively, whilst other elements preferentially form heteroligand complexes. Tetra- and pentadentate Pydc anions are found in the structures of elements of the sixth period and in complexes with a Pydc:$A < 2$ ratio. It has been concluded that when planning the synthesis of a heteroligand complex the structure of the initial complex and the comparative activity of all the ligands in substitution reactions should be taken into account.

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