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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF LITHIUM SALTS OF COPPER(II) AND NICKEL(II) COMPLEXES WITH 1,3-PROPANEDIAMINE-*N,N,N',N'*-TETRAACETATE

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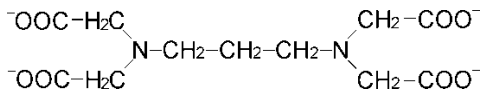
ABSTRACT

The complexes $Li_2[Ni(1,3\text{-pdta})]\cdot 5H_2O$ and $Li_2[Cu(1,3\text{-pdta})]\cdot 5H_2O$ (where 1,3-pdta represents the 1,3-propanediaminetetraacetate anion) have been synthesized and characterized by applying IR and UV-vis spectroscopy. The obtained spectroscopic results of these complexes are discussed in relation to those for $Mg[M(1,3\text{-pdta})].8H_2O$ complexes (M = Ni(II) and Cu(II)) of known crystal structure.

Keywords. Nickel(II) complexes, Copper(II) complexes, 1,3-pdta, IR spectroscopy, UV-vis spectrophotometry.

INTRODUCTION

The hexadentate 1,3-pdta ligand (1,3-pdta = 1,3-propanediamine-N,N,N',N'-tetraacetate anion) has been used for preparation of complexes with many transition metal ions (Herak et al., 1984; Rychlewska et al., 2000; Radanović et al., 2001; Radanović et al., 2003; Radanović et al., 2004; Rychlewska et al., 2005; Rychlewska et al., 2007; Rychlewska et al., 2011). In relation to edta (edta = ethylenediamine-N,N,N',N'-tetraacetate), the 1,3-pdta ligand has longer diamine chain and is expected to coordinate hexadentatedly to metal ions of various size.



1,3-pdta

The structural 1,3-pdta characteristics of the numerous hexadentate complexes of the type $M[M'(1,3\text{-pdta})]\cdot 8H_2O$ (M = Mg(II), Co(II), Zn(II), Sr(II); M' = Cu(II), Ni(II), Co(II), Mg(II), Zn(II) and Sr(II)) have been determined by single-crystal X-ray diffraction analysis (Rychlewska et al., 2000; Radanović et al., 2001; Radanović et al., 2003; Radanović et al., 2004; Rychlewska et al., 2005; Rychlewska et al., 2011). Previous attempts to isolate 1,3-pdta-M(II) complexes with monovalent cations as counter ion did not give the expected results. Recently, in our laboratory by ion exchange column chromatography, $Li_2[Co(1,3\text{-pdta})]\cdot 5H_2O$ complex was isolated (Rychlewska et al., 2008). This complex constitutes the first example of $[M(1,3\text{-pdta})]^{2-}$ complex with a monovalent cation as counter ion (Rychlewska et al., 2008). The structure of this complex consists of two tetrahedrally coordinated Li^+ cations, an octahedral $[Co(1,3\text{-pdta})]^{2-}$ anion and five water molecules, two of which are crystalline water molecules. As a continuation of our research, in the present paper, we report synthesis and spectroscopic characterization of two new Cu(II) and Ni(II) complexes with general formula $Li_2[M(1,3\text{-pdta})]\cdot 5H_2O$.

EXPERIMENTAL

Materials and methods

All commercially obtained reagent-grade chemicals were used without further purification. The preparation of $Ba_2(1,3\text{-pdta})\cdot 2H_2O$ has been reported elsewhere (Radanovic et al., 2000). The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using the KBr pellet technique. The UV-vis spectra of Ni(II) and Cu(II) complexes were recorded on a Perkin-Elmer spectrophotometer. The following concentrations of aqua solutions have been used for these measurements: 10^{-2} M for Ni(II) and 10^{-3} M for Cu(II) complexes. Elemental microanalysis for carbon, hydrogen and nitrogen were performed by the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, University of Belgrade.

*Synthesis of $Li_2[Ni(1,3\text{-pdta})]\cdot 5H_2O$ (**1**) and $Li_2[Cu(1,3\text{-pdta})]\cdot 5H_2O$ (**2**) complexes*

0.01 mol of $CuSO_4\cdot 5H_2O$ (2.50 g) or $NiSO_4\cdot 7H_2O$ (2.83 g) in 60 ml of H_2O was stirred at 80 °C for 10 min. To this solution, solid $Ba_2(1,3\text{-pdta})\cdot 2H_2O$ (6.13 g, 0.01 mol) was added and the obtained solution (pH = 7) was stirred at 80 °C for 3 h. The precipitated $BaSO_4$ was filtered off and to the obtained filtrate, the solid $MgSO_4\cdot 6H_2O$ (2.28 g; 0.01 mol) was added and stirring with heating at 60 °C was continued for the next 20 min. The precipitated $BaSO_4$ was again filtered off. To the obtained filtrate, 5–6 ml of ethanol was added and the solution was left to stand in a refrigerator for several days. The crystals of $Mg[Cu(1,3\text{-pdta})]\cdot 8H_2O$ (3.34 g, 66%) and $Mg[Ni(1,3\text{-pdta})]\cdot 8H_2O$ (3.38 g, 63%) were collected, washed with ethanol, then ether and air-dried.

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Anal. Calc. for Mg[Cu(1,3-pdta)]·8H_2O, $MgCuC_{11}H_{30}N_2O_{16}$ (FW = 534.21): C, 24.73; H, 5.66; N, 5.24%. Found: C, 24.84; H, 4.84; N, 5.04%.

Anal.Calc. for Mg[Ni(1,3pdta)]·8H_2O, $MgNiC_{11}H_{30}N_2O_{16}$ (FW = 529.36): C, 24.96; H, 5.71; N, 5.29%. Found: C, 24.90; H, 5.82; N, 5.32%.

The aqueous solutions of Mg[Ni(1,3pdta)]·8H_2O (Radanović et al., 2001) and Mg[Cu(1,3-pdta)]·8H_2O (Radanović et al., 2000) were passed through a column packed with Merck I cation exchanger in the Li^+ form. The eluates were evaporated at room temperature to a volume of 2 ml and Li_2[Ni(1,3-pdta)]·5H_2O **(1)** and Li_2[Cu(1,3-pdta)]·5H_2O **(2)** complexes were crystallized after addition of ethanol and cooling in a refrigerator for 2 days. The crystals were removed by filtration and air-dried.

Anal. Calc. for Li_2[Ni(1,3-pdta)]·5H_2O **(1)**, $Li_2NiC_{11}H_{24}N_2O_{13}$**(**FW = 464.89): C, 28.42; H, 5.20; N, 6.03. Found: C, 28.27; H, 5.22; N 6.05%.

Anal. Calc. for Li_2[Cu(1,3-pdta)]·5H_2O **(2)**, $Li_2CuC_{11}H_{24}N_2O_{13}$ (FW = 469.74): C, 28.13; H, 5.15; N, 5.96. Found: C, 27.93; H, 5.16; N, 5.96%.

RESULTS AND DISCUSSION

In this work two Li_2[M(1,3-pdta)]·5H_2O complexes (M = Ni(II), **1** and Cu(II), **2**) were synthesized and characterized by IR and UV-vis spectroscopy. The schematic presentation of the procedure for synthesis of **1** and **2** is presented in Figure 1. The spectroscopic results of these complexes are discussed in relation to those for Mg[Ni(1,3pdta)]·8H_2O and Mg[Cu(1,3-pdta)]·8H_2O complexes of known crystal structure (Radanović et al., 2001; Rychlewska et al., 2000).

*Comparative analysis of the spectroscopic data for **1** and **2** with those for Mg[Ni(1,3-pdta)]•8H_2O and Mg[Cu(1,3-pdta)]•8H_2O complexes of known crystal structure IR spectra*

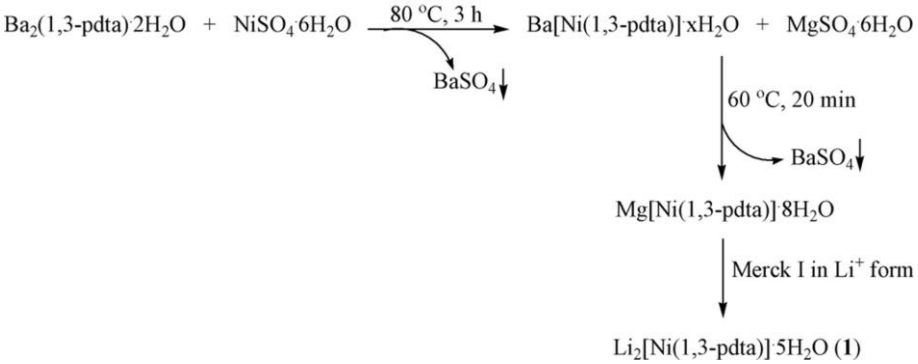

Figure 1. Schematic presentation of the procedure for the preparation of Li_2[Ni(1,3-pdta)]·5H_2O (**1**). The same method is used for the synthesis of Li_2[Cu(1,3-pdta)]·5H_2O (**2**).

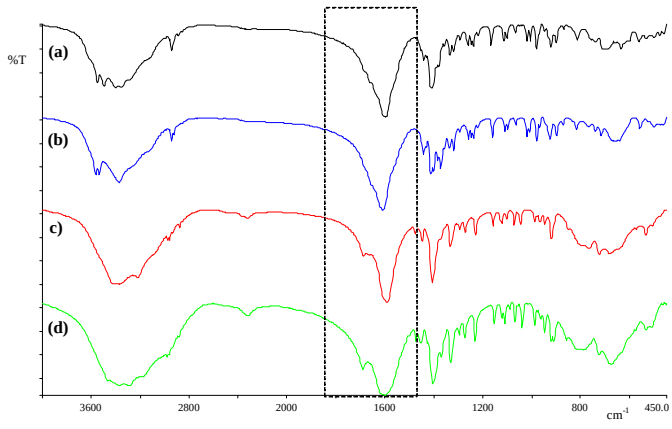

Figure 2. IR spectra of Ni(II) and Cu(II) complexes with hexadentate coordinated 1,3-pdta ligand: (a) Li_2[Ni(1,3-pdta)]·5H_2O **(1)**, (b) Li_2[Cu(1,3-pdta)]·5H_2O **(2)**, (c) Mg[Ni(1,3-pdta)]·8H_2O and (d) Mg[Cu(1,3-pdta)]·8H_2O.

The IR spectra of **1** and **2** are given in Figure 2. These spectra have been compared with the corresponding for Mg[Ni(1,3-pdta)]·8H_2O and Mg[Cu(1,3-pdta)]·8H_2O complexes having the same hexadentate coordinated 1,3-pdta ligand and Mg^{2+} ion as counter cation. The crystal structures of the latter two complexes have been previously determined by single crystal X-ray diffraction analysis (Radanović et al., 2001; Rychlewska et al., 2000). The IR data of these complexes, in the region for the asymmetric carboxylate stretching frequencies, are presented in Table 1. The interpretation of these spectra was done in accordance to the previously established rule that the protonated and uncoordinated asymmetric carboxylate stretching frequencies occur at 1750 – 1700 cm^{-1}, whereas these frequencies for the ionized and coordinated carboxylate groups are at 1650 – 1590 cm^{-1} (Nakamoto, 1963). As it was shown in Figure 2 and Table 1, complexes **1** and **2** in the region for the asymmetric carboxylate stretching frequencies have only one very strong and symmetric band at 1598 and 1610 cm^{-1}, respectively. This is in accordance to the fact that carboxylate groups of 1,3-pdta ligand in these two complexes are coordinated to the corresponding metal ion. Moreover, symmetric shape of these bands indicates that all glycinate rings in these complexes are equivalent. The IR spectra of **1** and **2** are very similar to those for Mg[Ni(1,3-pdta)]·8H_2O and Mg[Cu(1,3-pdta)]·8H_2O complexes. The latter two complexes in the carboxylate region

for coordinated glycinates showed very strong and broad band at 1590 and at 1599 cm^{-1} for Ni(II) and Cu(II) complexes, respectively (Table 1). Additionally, from Table 1 it can be seen that these two bands are slightly shifted to the higher energy in respect to those for complexes **1** and **2**. Moreover, the carboxylate stretching band for Mg[Ni(1,3-pdta)]·$8H_2O$ and Mg[Cu(1,3-pdta)]·$8H_2O$ complexes showed evidence for splitting on the higher energy side resulting in appearance of small band at 1688 for Ni(II) and 1692 cm^{-1} for Cu(II) complex.

Table 1. IR asymmetric carboxylate stretching frequencies of Ni(II) and Cu(II) complexes with 1,3-pdta ligand

Complex	**ν_{asym} (cm^{-1})**
Li_2[Ni(1,3-pdta)]·$5H_2O$ **(1)**	1598
Li_2[Cu(1,3-pdta)]·$5H_2O$ **(2)**	1610
Mg[Ni(1,3-pdta)]·$8H_2O$	1590; 1688(sh)
Mg[Cu(1,3-pdta)]·$8H_2O$	1599; 1691(sh)

UV-vis spectra

Difference in the position and shape of the asymmetric carboxylate stretching frequencies for **1** and **2** in respect to those for Mg[Ni(1,3-pdta)]·$8H_2O$ and Mg[Cu(1,3-pdta)]·$8H_2O$ can be attributed to the presence of different counter cation in these two pairs of 1,3-pdta complexes. The presence of different cation in these complexes can result in their different packing in the crystal lattice as well as in different interactions between coordinated water molecules of Li^+ and Mg^{2+} counter cation and carboxylate group of $[M(1,3\text{-pdta})]^{2-}$ complex anion (M = Ni(II) and Cu(II)).

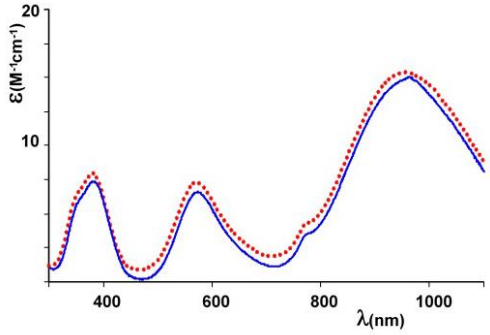

Figure 3. UV-vis spectra of **1** (···) and Mg[Ni(1,3-pdta)]·$8H_2O$ (Radanović et al., 2001).

The UV-vis spectra of **1** and Mg[Ni(1,3pdta)]·$8H_2O$ complexes and their numerical data are presented in Figure 3. and Table 2. The UV-vis spectrum of Mg[Ni(1,3-pdta)]·$8H_2O$ has been previously discussed in detail (Radanović et al., 2001), and here it has only been repeated for the sake of comparison with the spectrum of **1**. In general, it has been shown that the spectra of Ni(II)-1,3-pdta-type complexes containing the six-membered diamine ring (**T** ring), with respect to Ni(II)-edta-type complexes with five-membered diamine ring (**E** ring), exhibit broadening of the first absorption band(D_{4h} model) (Radanović et al., 2001).

In accordance to previously established results for the Ni(II)-edta-type and most other Ni(II) complexes, the interpretation of the UV-vis spectra of **1** and Mg[Ni(1,3-pdta)]·$8H_2O$ (Radanović et al., 2001) has been done by using an octahedral model (O_h): $^3A_{2g}\rightarrow{}^3T_{2g}$ (*F*) (band I); $^3A_{2g}\rightarrow{}^3T_{1g}$ (*F*) (band III) and $^3A_{2g}\rightarrow{}^3T_{1g}$ (*P*) (band IV) (Table 2). From Figure 3 it can be seen that UV-vis spectra of **1** and Mg[Ni(1,3-pdta)]·$8H_2O$ (Radanović et al., 2001) are almost identical in the shape and intensities of absorption maxima. This undoubtedly leads to the conclusion that anionic part of these two molecules are the same and represents octahedral complex containing hexadentate coordinated 1,3-pdta ligand. As it was abovementioned, the influence of counter cation on the shape and position of the carboxylate stretching frequencies was observed after measuring IR spectra of these complexes in the solid state. However, no influence of Li^+ and Mg^{2+} counter cation was observed on the shape and position of absorption maxima in the UV-vis spectra of these complexes measured in water solvent.

UV-vis spectra of **2** and Mg[Cu(1,3-pdta)]·$8H_2O$ (Rychlewska et al., 2000) and corresponding numerical data are given in Figure 4 and Table 2. The UV-vis spectrum of Mg[Cu(1,3-pdta)]·$8H_2O$ complex has been previously reported (Rychlewska et al., 2000) and, in the present work, it has been repeated for comparison with the spectrum of **2**. As it can be seen from Figure 4, complexes **2** and Mg[Cu(1,3-pdta)]·$8H_2O$ have one unsymmetrical absorption band in the expected region, what is in accordance to the fact that these complexes have the same N_2O_4 donor system and C_2 molecular symmetry.

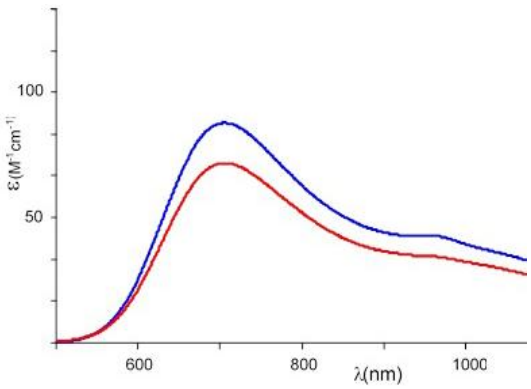

Figure 4. UV-vis spectra of **2** and Mg[Cu(1,3-pdta)]·$8H_2O$ (Rychlewska et al., 2000).

This band can be assigned to the d_z^2, d_{xy}, d_{xz}, $d_{yx}\rightarrow d_{x^2-y^2}$ transitions with a $d_{x^2-y^2}$ ground state. The UV-vis spectra of **2** and Mg[Cu(1,3-pdta)]·$8H_2O$ complexes are identical in the position of the absorption maxima. However, there is small difference in the intensity of these absorption bands resulted in

the presence of different counter cation and number of water molecules in these two complexes.

Table 2. UV-vis numerical data of **1** and **2** in comparison to those for $Mg[Ni(1,3\text{-pdta})]\cdot 8H_2O$ (Radanović et al., 2001) and $Mg[Cu(1,3\text{-pdta})]\cdot 8H_2O$ (Rychlewska et al., 2000) complexes with hexadentate 1,3-pdta ligand

Complex	Absorption			Assignments
		λ (nm)	ε ($M^{-1}cm^{-1}$)	O_h
$Mg[Ni(1,3\text{-pdta})]\cdot 8H_2O$	I	959.9	15.4	$^3A_{2g}\rightarrow{}^3T_{2g}(F)$
	II	770.3	3.9	$\rightarrow{}^1E_g(D)$
	III	571.5	7.3	$\rightarrow{}^3T_{1g}(F)$
	IV	379.7 (sh)	7.9	$\rightarrow{}^3T_{1g}(P)$
$Li_2[Ni(1,3\text{-pdta})]\cdot 5H_2O$ (**1**)	I	962.1	15.8	
	II	775.6	4.1	
	III	573.2	7.3	
	IV	380.9	8.2	
$Mg[Cu(1,3\text{-pdta})]\cdot 8H_2O$		706.0	85.0	
$Li_2[Cu(1,3\text{-pdta})]\cdot 5H_2O$ **(2)**		705.1	86.0	

CONCLUSION

In this paper, the new method for preparation of $[Ni(1,3\text{-pdta})]^{2-}$ (**1**) and $[Cu(1,3\text{-pdta})]^{2-}$ (**2**) complexes with Li^+ counter cation has been presented. The hexadentate coordination of 1,3-pdta ligand in these complexes was confirmed by comparison of their IR and UV-vis spectra with those for $Mg[Ni(1,3\text{-pdta})]\bullet 8H_2O$ and $Mg[Cu(1,3\text{-pdta})]\bullet 8H_2O$ complexes of known crystal structure (Radanović et al., 2001; Rychlewska et al., 2000). The IR spectra of **1** and **2** are slightly different from those for $Mg[Ni(1,3\text{-pdta})]\bullet 8H_2O$ and $Mg[Cu(1,3\text{-pdta})]\bullet 8H_2O$ complexes, what can be attributed to the presence of different counter cation in these two pairs of 1,3-pdta complexes. On the other hand, no difference in the UV-vis spectra of these complexes was observed.

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REFERENCES

Nakamoto, K. 1963. Infrared Spectra of Inorganic and Coordination Compounds. New York, N. Y.: John Wiley & Sons, Inc..

Herak, R., Srdanov, G., Djuran, M.I., Radanović, D.J., & Bruvo, M. 1984. Crystal structures of $Na[M(1,3\text{-pdta})]\cdot 3H_2O$ (M = Cr, Rh;1,3-pdta = 1,3-propanediaminetetraacetate), and the absolute configuration of the (-)D-Isomer of the Rh complex. Inorg. Chim. Acta, 83, pp. 55-64.

Radanović, D.J., Ama, T., Kawaguchi, H., Drašković, N.S., Ristanović, D., & Janićijević, S. 2001. Synthesis and X-Ray Structural Study of Magnesium (1,3-propanediaminetetraacetato)nickelate(II) Octahydrate, $Mg[Ni(1,3\text{-pdta})]\cdot 8H_2O$. Structural Parameters and Strain Analysis of $[M(1,3\text{-pdta})]_n$: Complexes in Relation to Their Octahedral Distortion. Bull. Chem. Soc. Jpn., 74, pp. 701-706.

Radanović, D.D., Rychlewska, U., Djuran, M.I., Drašković, N.S., Vasojević, M., Hodžić, I., & Radanović, D.J. 2003. Simple synthetic method and structural characteristics of (1,3-propanediaminetetraacetato)cobalt(II) complexes: Uniform crystal packing in a series of metal(II) complexes with 1,3-propanediaminetetraacetate ligand. Polyhedron, 22, pp. 2745-2753.

Radanović, D.D., Rychlewska, U., Djuran, M.I., Warżajtis, B., Drašković, N.S., & Gurešić, D.M. 2004. Alkaline earth metal complexes of the edta-type with a six-membered diamine chelate ring: Crystal structures of $[Mg(H_2O)_6][Mg(1,3\text{-pdta})]\cdot 2H_2O$ and $[Ca(H_2O)_3Ca(1,3\text{-pdta})(H_2O)]\cdot 2H_2O$: Comparative stereochemistry of edta-type complexes. Polyhedron, 23, pp. 2183-2192.

Rychlewska, U., Radanović, D.D., Jevtović, V.S., & Radanović, D.J. 2000. Synthesis and X-ray structural study of magnesium (1,3-propanediaminetetraacetato)-cuprate(II) octahydrate, $Mg[Cu(1,3\text{-pdta})]\cdot 8H_2O$.: Stereochemistry of hexadentate copper(II)–edta-type complexes in relation to the structure of the ligand. Polyhedron, 19, pp. 1-5.

Rychlewska, U., Gurešić, D.M., Warżajtis, B., Radanović, D.D., & Djuran, M.I. 2005. Highly selective crystallization of metal(II) ions with 1,3-pdta ligand: Syntheses and crystal structures of the $[Mg(H_2O)_6][Cd(1,3\text{-pdta})(H_2O)]\cdot 2H_2O$ and two isomorphic $[Zn(1,3\text{-pdta})]^{2-}$ complexes. Polyhedron, 24, pp. 2009-2016.

Rychlewska, U., Warżajtis, B., Cvetić, D., Radanović, D.D., Gurešić, D.M., & Djuran, M.I. 2007. Two distinct manganese(II) complexes with hexadentate 1,3-propanediaminetetraacetate ligand: The ability of metal(II) complexes with 1,3-pdta ligand to form solid solutions. Polyhedron, 26, pp. 1717-1724.

Rychlewska, U., Wazajtis, B., Radanovic, D.D., Draškovic, N.S., Stanojevic, I.M., & Djuran, M.I. 2011. Structural diversification of the coordination mode of divalent metals with 1,3-propanediaminetetraacetate (1,3-pdta): The missing crystal structure of the s-block metal complex $[Sr_2(1,3\text{-pdta})(H_2O)_6]\cdot H_2O$. Polyhedron, 30(6), pp. 983-989.

Rychlewska, U., Warżajtis, B., Djuran, M.I., Radanović, D.D., Dimitrijević, M., & Rajković, S. 2008. Coordination behaviour and two-dimensional-network formation in poly[[μ-aqua-di-aqua(μ5-propane-1,3-diyldinitrilotetraacetato)dilithium(I)-cobalt(II)] dihydrate]: The first example of an M^{II}-1,3-pdta complex with a monovalent metal counter-ion. Acta Cryst C.,64, pp. 217-220.