

$\frac{1}{2}[\text{M}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ (M = Cu, Cd; O₂C-C₆H₄-CO₂ = benzene-1,4-dicarboxylate, terephthalate): 1D Coordination Polymers with Strong Inter-Chain Hydrogen Bonding

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Abstract. Compounds $\frac{1}{2}[\text{M}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ crystallize as straight- (M = Cu) and kinked-chain (M = Cd) coordination polymers through the bridging action of the bis-mono (Cu) and bis-bidentate (Cd) benzene-1,4-dicarboxylate (terephthalate) ligand. N-H...O hydrogen bonding connects the chains to a three-dimensional supramolecular network. Thermogravimetry shows the compounds to be stable up to 255 °C (M = Cu) and 70 °C (M = Cd) where

decomposition starts with the loss of one ammin ligand. $\frac{1}{2}[\text{Cd}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ exhibits a luminescence with $\lambda_{\text{em,max}} = 392$ nm ($\lambda_{\text{ex}} = 240$ nm) on the same order of magnitude as $\text{Na}_2(\text{O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)$.

Keywords: Coordination polymers; Terephthalate; Benzene-1,4-dicarboxylate; Thermogravimetry; Luminescence

$\frac{1}{2}[\text{M}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ (M = Cu, Cd; O₂C-C₆H₄-CO₂ = Benzol-1,4-dicarboxylat, Terephthalat): 1D-Koordinationspolymere mit starken H-Brücken zwischen den Ketten

Inhaltsübersicht. Die Verbindungen $\frac{1}{2}[\text{M}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ kristallisieren als Koordinationspolymere mit geraden (M = Cu) oder gewinkelten Ketten (M = Cd) durch die Verbrückung des bis-ein- (Cu) oder bis-zweizähligen (Cd) Benzol-1,4-dicarboxylat-(Terephthalat-)Liganden. N-H...O-Wasserstoffbrücken verknüpfen die Ketten zu einem dreidimensionalen supramolekularen Netzwerk. Thermogravimetrische Messungen zeigen die Stabilität der

Verbindungen bis zu einer Temperatur von 255 °C (M = Cu) oder 70 °C (M = Cd) wo Zersetzung mit dem Verlust eines Ammin-Liganden beginnt. Die Verbindung $\frac{1}{2}[\text{Cd}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ zeigt Lumineszenz mit $\lambda_{\text{em,max}} = 392$ nm ($\lambda_{\text{ex}} = 240$ nm) und einer Intensität in der gleichen Größenordnung wie $\text{Na}_2(\text{O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)$.

Introduction

Metal-organic networks or coordination polymers recently attract much attention because of topology design and potential properties in adsorption, catalysis, luminescence, magnetism etc. [1–3]. In particular aromatic dicarboxylate ligands, with terephthalate (benzene-1,4-dicarboxylate, bdc) being one of the simplest member of this series, feature prominently as bridging ligands in the construction of highly porous and robust metal-organic (carboxylate) frameworks [4, 5]. We describe here the structures and thermal stabilities of two one-dimensional (1D) metal-terephthalate coordination polymers with strong N-H...O interchain bonding leading to three-dimensional supramolecular networks.

In $\frac{1}{2}[\text{Cu}(\mu\text{-bdc})(\text{NH}_3)_2]$ (1, Fig. 1) the Cu^{II} ion is coordinated square-planar in a *trans* configuration by two ammin and two bis-monodentate terephthalato ligands. The Jahn-Teller distortion manifests itself towards additional long contacts to the second oxygen atom of each pseudo-chelating carboxyl group. The *trans*-arranged terephthalato ligands bridge between the metal ions to a straight-chain polymer. Other 1D Cu-terephthalate structures have bidentate chelating nitrogen ligands so that the benzene-1,4-di-

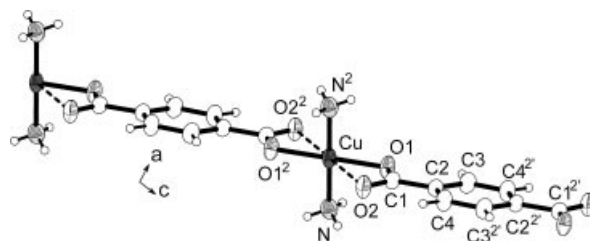


Fig. 1 Straight-chain structure of $\frac{1}{2}[\text{Cu}(\mu\text{-bdc})(\text{NH}_3)_2]$ in 1.

Selected distances/Å and angles/°: Cu-O1 1.961(2), Cu-N 1.989(2), Cu-O2 2.738(2), O1-Cu-N 87.99(9), O1-C-N² 92.01(9), symmetry operation: ² = -x+1, -y+1, -z; ^{2'} = -x+2, -y+2, -z+1.

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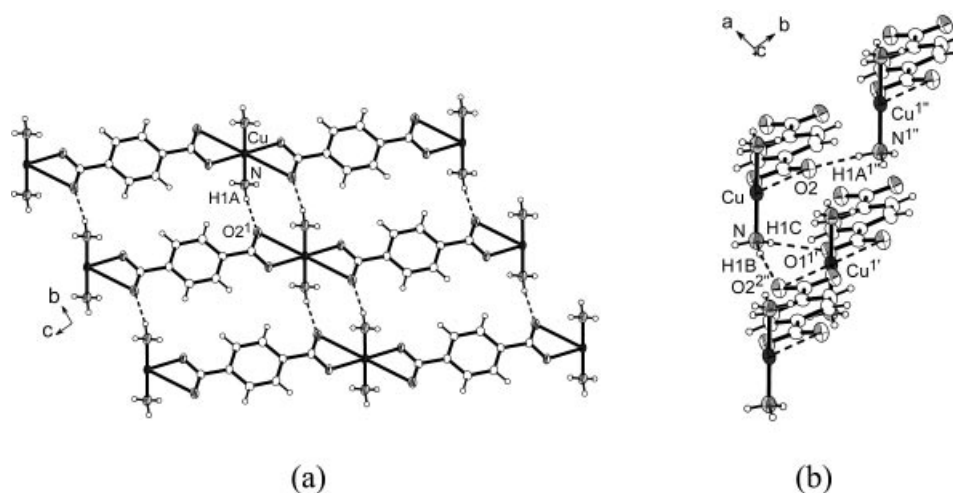


Fig. 2 Hydrogen bonding between the $\frac{1}{2}\{[\text{Cu}(\mu\text{-bdc})(\text{NH}_3)_2]\}$ -chains in **1** (a) along *b*, that is within the *bc* plane, and (b) along *a* and *b*; see Table 1 for details; symmetry operations $^1 = x, y-1, z$; $^{1'} = x-1, y, z$; $^{1''} = x, y+1, z$; $^{2''} = -x, -y+1, -z$.

Table 1 Hydrogen-bonding interactions in **1**.

D-H...A ^{a)}	D-H /Å	H...A /Å	D...A /Å	D-H...A /°
N-H1A...O2 ¹	0.90(3)	2.08(3)	2.966(3)	170(3)
N-H1B...O2 ^{2''}	0.78(3)	2.42(3)	3.191(3)	171(3)
N-H1C...O1 ^{1'}	0.76(3)	2.38(3)	3.066(3)	151(3)

^{a)} Symmetry operations: $^1 = x, y-1, z$; $^{1'} = x-1, y, z$; $^{2''} = -x, -y+1, -z$.

carboxylate (bdc) bridges are forced into a *cis*-position to each other, thereby resulting in zig-zag chain (cf. compound **2**) [6, 7, 8].

The chains in **1** are interconnected through N-H...O hydrogen bonds from the ammin to the terephthalato ligands to yield an overall three-dimensional network based on a 1D coordination polymer and extended by supramolecular hydrogen bonding (Fig. 2). Related hydrogen-bonded networks are formed between the Cu-ligand chains in $\frac{1}{2}\{[\text{Cu}(\mu\text{-bdc})(1,10\text{-phen})(\text{H}_2\text{O})](\text{H}_2\text{O})(\text{dmf})\}$ [6] and in $\frac{1}{2}\{[\text{Cu}(\mu\text{-btecH}_2)(\text{H}_2\text{O})_3](\text{H}_2\text{O})_3\}$ (btec = benzene-1,2,4,5-tetracarboxylate) [9] and the Cu-ligand nets in $\frac{2}{3}\{[\text{Cu}(\mu\text{-bdc})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})]\}$ [10]. The latter three structures feature square-pyramidal coordinated metal ions.

A thermogravimetric analysis (TGA) of **1** (Fig. 3) shows the first weight loss at 255 °C (6.5 %) corresponding to the removal of one ammonia molecule per formula unit (6.5 % calc.). The second weight loss at 280 °C (6.5 %) matches the removal of the second ammin ligand (6.5 % theor.). The third mass loss at 375 °C (41.0 %) is due to the decomposition of the terephthalato ligand into carbon dioxide (30.6 % theor.), carbon monoxide, hydrocarbons and carbonous material [11]. The residue appears to consist of the metal and a noticeable amount of carbonous material.

In $\frac{1}{2}[\text{Cd}(\mu\text{-bdc})(\text{NH}_3)_2]$ (**2**) the Cd(II) ion is trigonal-prismatic coordinated in a *cis*-configuration by two ammin and two bis-bidentate terephthalato ligands (Fig. 4).

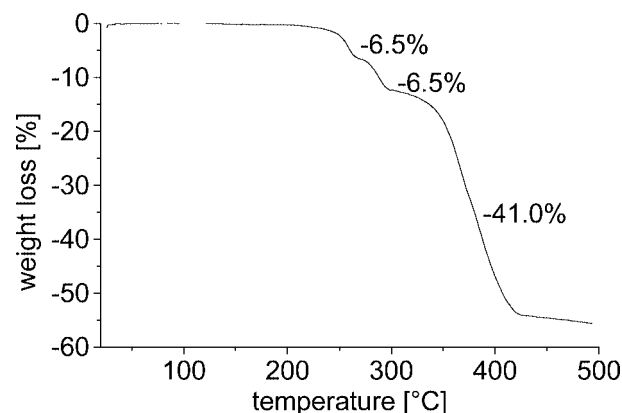


Fig. 3 TGA curve of $\frac{1}{2}[\text{Cu}(\mu\text{-bdc})(\text{NH}_3)_2]$ (**1**).

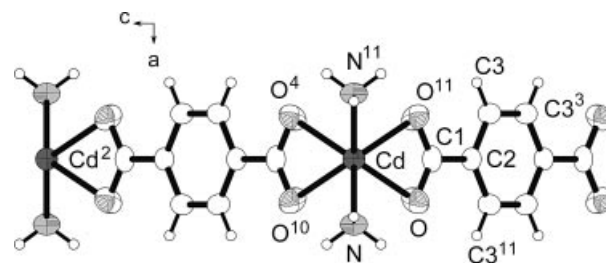


Fig. 4 Zig-zag-chain structure of $\frac{1}{2}[\text{Cd}(\mu\text{-bdc})(\text{NH}_3)_2]$ in **2**.

Selected distances/Å and angles/°: Cd-O 2.385(2), Cd-N 2.251(3), N-Cd-N¹¹ 99.6(2), N-Cd-O 91.37(9), N-Cd-O¹¹ 136.25(6), O-Cd-O¹¹ 54.4(1), O-Cd-O¹⁰ 85.05(11), O-Cd-O⁴ 109.4(1), symmetry operations $^2 = -x, -y, z+1/2$; $^3 = x, -y, -z$; $^4 = -x, y, -z+1/2$; $^{10} = x, y, -z+1/2$; $^{11} = -x, y, z$.

The zig-zag chains in **2** are interconnected through N-H...O hydrogen bonds between the ammin and the terephthalato ligands to again yield an overall 3D network based on the 1D coordination polymer which is extended by supramolecular hydrogen bonding (Fig. 5).

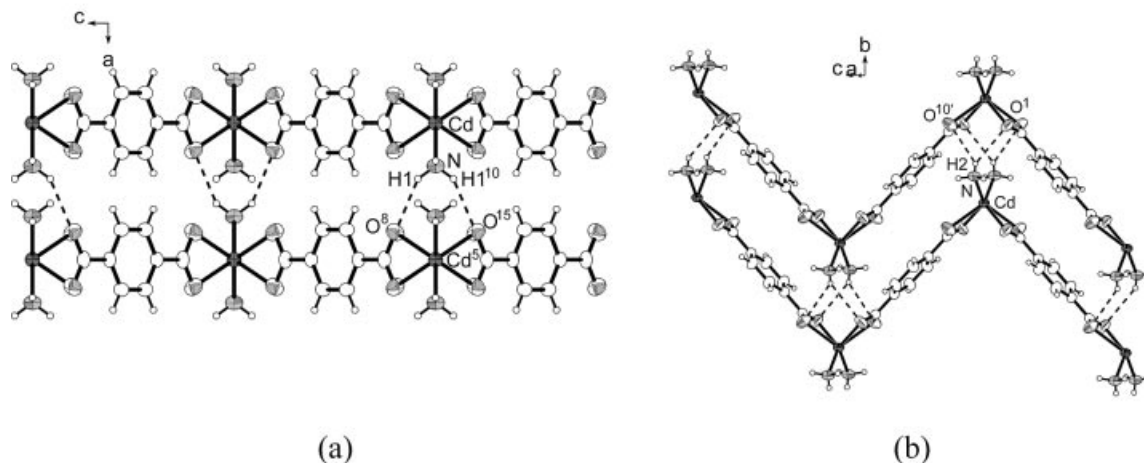


Fig. 5 Hydrogen bonding between the $\frac{1}{2}[\text{Cd}(\mu\text{-bdc})(\text{NH}_3)_2]$ -chains in **2** (a) along a and (b) along b ; see Table 1 for details, symmetry operations: $^1 = x, y+1, z$; $^5 = x+1/2, y+1/2, z$; $^8 = -x+1/2, y+1/2, -z+1/2$; $^{10} = x, y, -z+1/2$; $^{10'} = x, y+1, -z+1/2$; $^{15} = -x+1/2, y+1/2, z$.

Table 2 Hydrogen-bonding interactions in **2**.

D-H...A ^{a)}	D-H /Å	H...A /Å	D...A /Å	D-H...A /°
N-H1...O ⁸	0.88(3)	2.32(3)	3.107(4)	148(3)
N-H2...O ^{10'}	0.70(5)	2.65(4)	3.235(4)	142(9)
N-H2...O ¹	0.70(5)	2.65(4)	3.235(4)	142(9)

^{a)} Symmetry operations: $^1 = x, y+1, z$; $^8 = -x+1/2, y+1/2, -z+1/2$; $^{10'} = x, y, -z+1/2$.

With respect to the zig-zag chain structure in **2** similar chains are found in $\frac{1}{2}[\text{Cd}(\mu\text{-bdc})(\text{H}_2\text{O})_3 \cdot (\text{H}_2\text{O})_4]$ albeit with a more complicated hydrogen-bonding network [12] or in $\frac{3}{2}[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{Cd}(\mu\text{-bdc})\text{Cl}] \cdot (\text{H}_2\text{O})_2$ as part of a 3D framework with the bridging chloro ligands [13]. Other terephthalato-bridged cadmium coordination polymers contain tetrakis-monodentate (in $\frac{3}{2}[\text{Cd}(\mu_4\text{-bdc})_{1/2}\text{Cl}(1,10\text{-phen})]$ [14]) or bis-tridentate terephthalato ligands (in $\frac{3}{2}[\text{Cd}(\mu_4\text{-bdc})(\text{pyridine})]$ [15]) bridging between four cadmium ions as part of a 3D framework. Noteworthy, the last two structures have been obtained through hydrothermal reactions from 1,4-dicyanobenzene by its slow hydrolysis into terephthalic acid [14, 15].

A thermogravimetric analysis of **2** (Fig. 6) shows the first weight loss at 70 °C (6.5%) corresponding to the removal of one ammonia molecule per formula unit (5.5% calc.). The second weight loss at 240 °C (6%) matches the removal of the second ammin ligand (5.5% theor.). The third mass loss at 440 °C (34.0%) is due to the decomposition of the terephthalato ligand (CO₂ theor. 25.8%) [11]. The residue appears to consist of the metal and a noticeable amount of carbonous material.

Coordination polymers are studied for luminescence properties owing to their often higher thermal stability than the pure organic ligand and the ability of affecting the emission wavelength of the ligand by metal coordination [1].

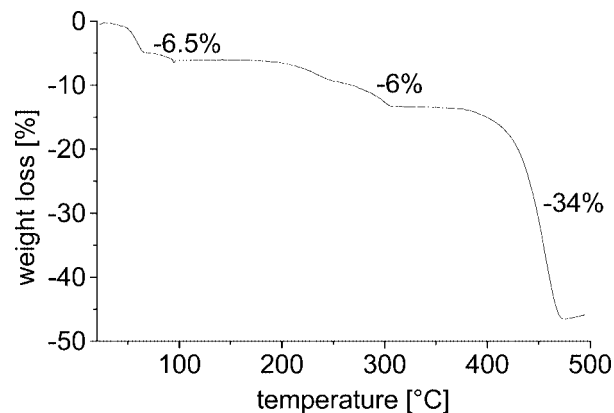


Fig. 6 TGA curve of $\frac{1}{2}[\text{Cd}(\mu\text{-bdc})(\text{NH}_3)_2]$ (**2**).

Compound $\frac{1}{2}[\text{Cd}(\mu\text{-bdc})(\text{NH}_3)_2]$ (**2**) but not the Cu analog **1** exhibits luminescence in the same wavelength region and on at least the same order of magnitude if not stronger than free terephthalic acid or its disodium salt. The absorption spectrum of **2** in diffuse reflectance mode shows two maxima at 237 and 288 nm (Fig. 7a). The luminescence spectrum of **2** exhibits an emission maximum at 392 nm and a shoulder at 420 nm upon excitation at 240 nm (Fig. 7b), essentially unshifted from the maximum for free terephthalic acid ($\lambda_{\text{em,max}} = 389$ nm) or its disodium salt ($\lambda_{\text{em,max}} = 385$ nm). Because of the unchanged emission wavelength the luminescence is assigned to intraligand transitions. The concomitant excitation spectrum (Fig. 7c, collected at the emission wavelength of 420 nm) reveals a mirror-image like absorption at 342 nm with a shoulder at 330 nm. The luminescence intensity of **2** seems somewhat stronger than in disodium terephthalate and even more so than in the free acid. Still in the complex $\frac{3}{2}[\text{Cd}(\mu_4\text{-bdc})(\text{pyridine})]$ [15] the emission intensity was enhanced about 100

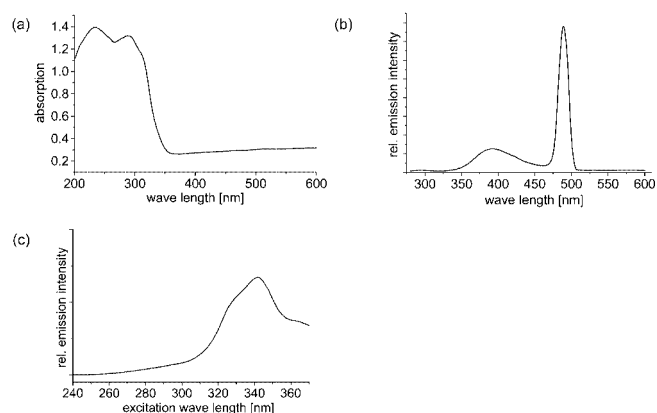


Fig. 7 Optical spectra of $[\text{Cd}(\mu\text{-bdc})(\text{NH}_3)_2]$ (**2**): (a) Diffusion reflectance absorption spectrum, (b) emission spectrum with $\lambda_{\text{ex}} = 240$ nm (the sharp peak at 480 nm is the second harmonic transition), (c) excitation spectrum collected at $\lambda_{\text{em}} = 420$ nm.

times over that of the free terephthalate ligand, probably due to a symmetry decrease by serious ligand twisting.

Experimental

Elemental analyses were obtained on a VarioEL from Elementar-analysensysteme GmbH. IR spectra (2–4 mg compound/300 mg KBr pellet) were measured on a Bruker Optik IFS25. NMR spectra were collected on a Bruker ARX200 (200 MHz for ^1H) with calibration against the residual protonated solvent signal (DMSO 2.52 ppm). Dissolution of the coordination polymeric compounds

for the NMR study means disintegration into the metal and ligand building blocks. Thermogravimetric analyses were carried out on a simultaneous thermoanalysis apparatus STA 409 from Netzsch under nitrogen (heating rate 5 K min^{-1}). The diffuse reflectance spectrum was measured on a Perkin-Elmer Lambda 900 spectrophotometer with an integrating sphere against a white standard. Emission spectra were measured on a Perkin-Elmer LS-50B ($\lambda_{\text{ex}} = 240$ nm, split widths (em, ex) 5.0 nm, scan speed 2 nm s^{-1} , sample in quartz capillary) or together with the excitation spectrum on an SLM-Aminco 8100 (split widths 16 nm, scan speed 0.5 nm s^{-1}). All optical spectra were collected with powders at room temperature.

General Procedure for the Preparation of $[\text{M}(\mu\text{-bdc})(\text{NH}_3)_2]$:

A solution of $\text{M}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_n$ (3.24 mmol, $\text{M} = \text{Cu}^{2+}$, $n = 3$; Cd^{2+} , $n = 4$) in MeOH (5 ml) was combined with a solution of ammonia (26 %, 15 ml). The solvent was then allowed to evaporate slowly at room temperature. After several days crystals formed which were suitable for X-ray single crystal analysis.

catena-polydiammin(μ-benzene-1,4-dicarboxylato-κ²O¹:O⁴)copper(II), $[\text{Cu}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ (**1**). Blue-violet isometric crystals, yield 14.0 mg, 53 %. Calc. for $\text{C}_8\text{H}_{10}\text{CuN}_2\text{O}_4$ (261.73): C 36.71, H 3.85, N 10.70. Found C 36.58, H 3.91, N 10.68 %.

IR (cm^{-1}): 3343m, 3320m, 3265m, 3239m, 3158m, 1946w, 1641m, 1622m, 1569s, 1500m, 1400m, 1380s, 1355s, 1317m, 1300m, 1234m, 1144m, 1103w, 1012m, 880w, 837m, 742m, 711m, 584m, 494m.

¹H-NMR: (DMSO-*d*₆/HCl): δ 7.94 (s).

catena-polydiammin(μ-benzene-1,4-dicarboxylato-κ⁴O¹,O¹:O⁴,O⁴)-cadmium(II), $[\text{Cd}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ (**2**). Colorless plates, yield 23.0 mg, 74 %. Calc. for $\text{C}_8\text{H}_{10}\text{CdN}_2\text{O}_4$ (310.59): C 30.94, H 3.25, N 9.02. Found: C 30.80, H 3.34, N 8.80 %.

Table 3 Crystal data and structure refinement for compounds **1** and **2**.

Compound	$[\text{Cu}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ (1)	$[\text{Cd}(\mu\text{-O}_2\text{C-C}_6\text{H}_4\text{-CO}_2)(\text{NH}_3)_2]$ (2)
Empirical formula	$\text{C}_8\text{H}_{10}\text{CuN}_2\text{O}_4$	$\text{C}_8\text{H}_{10}\text{CdN}_2\text{O}_4$
<i>M</i> / (g mol ⁻¹)	261.73	310.59
Crystal size / mm	$0.12 \times 0.07 \times 0.04$	$0.15 \times 0.12 \times 0.03$
θ Range / °	2.11 – 28.46	2.53 – 28.82
<i>h</i> ; <i>k</i> ; <i>l</i> range	–5, 5; –7, 8; –13, 13	–14, 14; –7, 7; –20, 20
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	<i>Cmcm</i>
<i>a</i> / Å	4.090(3)	10.931(7)
<i>b</i> / Å	6.037(4)	5.565(3)
<i>c</i> / Å	9.822(7)	16.112(10)
α / °	93.57(1)	
β / °	99.19(1)	
γ / °	100.16(1)	
<i>V</i> / Å ³	234.6(3)	980(1)
<i>Z</i>	1	4
<i>D</i> _{calc} / (g cm ⁻³)	1.852	2.105
<i>F</i> (000)	133	608
μ / mm ⁻¹	2.322	2.223
Max/min transmission	0.9129/0.7680	0.9363/0.7315
Reflections collected	1975	4210
Unique reflections (<i>R</i> _{int})	1070 (0.0160)	674 (0.0372)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	997	597
Parameters refined	79	46
Max./min. Δρ ^{a)} (e Å ⁻³)	0.478/–0.547	0.853/–0.802
<i>R</i> 1/ <i>wR</i> 2 ^{b)} [<i>I</i> > 2σ(<i>I</i>)]	0.0277/0.0670	0.0245/0.0555
<i>R</i> 1/ <i>wR</i> 2 ^{b)} (all data)	0.0297/0.0679	0.0288/0.0568
Goodness-of-fit on <i>F</i> ^{2c)}	1.018	1.055
Weighting scheme <i>w</i> ; <i>a/b</i> ^{d)}	0.0409/0.0000	0.0328/0.0000

^{a)} Largest difference peak and hole. – ^{b)} $R_1 = [\sum(|F_o| - |F_c|)] / \sum F_o$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$ – ^{c)} Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$ – ^{d)} $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2) / 3$

IR (cm⁻¹): 3342m, 3260m, 3245m, 1567s, 1503m, 1397s, 1377m, 1299m, 1213m, 1110m, 1011m, 887m, 839m, 745m, 573m, 522m.
¹H-NMR: (DMSO-d₆/HCl): δ 7.96 (s).

Structure determinations

Data Collection: Bruker AXS with CCD area-detector, temperature 233(2) K, Mo-K α radiation ($\lambda = 0.71073$ Å), graphite monochromator, double-pass method ϕ - ω -scan, Data collection and cell refinement with SMART [16], data reduction with SAINT [16], experimental absorption correction with SADABS [17]. **Structure Analysis and Refinement:** The structure was solved by direct methods (SHELXS-97) [18]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [18].

All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms on the aromatic ring were placed at calculated positions with an appropriate riding model (AFIX 43) and an isotropic temperature factor of $U_{eq} = 1.2 U_{eq}(C)$. The hydrogen atoms of the ammin ligand were found and refined with $U_{eq} = 1.5 U_{eq}(N)$.

Graphics were obtained with DIAMOND [19]. Displacement ellipsoids are drawn at the 70 % (1) and 50 % (2) probability level and H atoms are shown as spheres of arbitrary radii. Crystal data and details on the structure refinement are given in Table 3. The structural data have been deposited with the Cambridge Crystallographic Data Center (No. 244887 for 1, CCDC-244886 for 2).

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