Electronic Supplementary Material (ESI) for Dalton Transactions

Synthesis and characterization of Co(III) amidoamine complexes: Influence of substituents of the ligand on catalytic cyclic carbonate synthesis from epoxide and carbon dioxide

Punnamchandar Ramidi[1], Nikolay Gerasimchuk[2], Yashraj Gartia[1], Charlette M. Felton[1] and Anindya Ghosh[1,*]

[1] *Department of Chemistry, University of Arkansas at Little Rock, 2801 South University Avenue, Little Rock, AR 72204, USA*

[2] *Department of Chemistry, Temple Hall 456, Missouri State University, Springfield, Missouri 65897*

*Corresponding author: E-mail: axghosh@ualr.edu, Phone: 501 569 8827, Fax: 501 569 8838

***Materials*:** All the chemicals and solvents were obtained either from Aldrich Chemical Co. USA or Fisher Scientific Company, USA and used as obtained without further purifications unless otherwise stated. Tetrahydrofuran (THF) was purified using sodium and benzoephenone.[1]

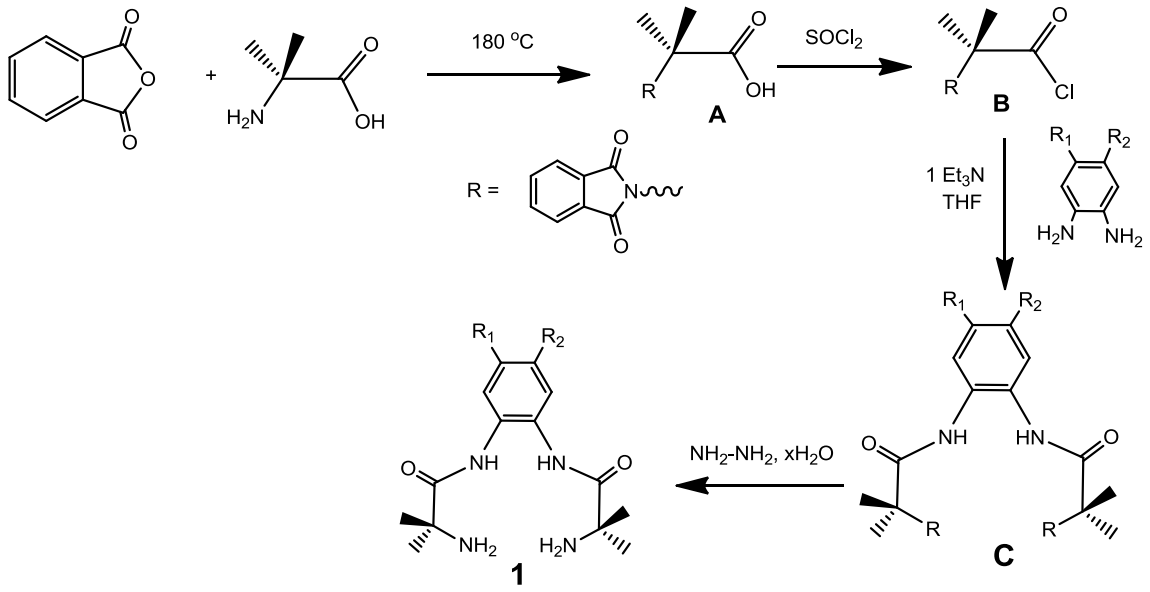
***Physical Measurements*:** ^{1}H and ^{13}C-NMR spectra were obtained either using a 600 MHz Bruker or a JEOL 400 MHz ECS 400 instrument equipped with a 5 mm triple resonance inverse probe. The spectra were collected at 25 °C and chemical shifts are in ppm relative to TMS as external standard unless otherwise stated. Infrared spectra were obtained on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed by Midwest Microlab, Indianapolis. Electrospray ionization mass spectra (ESI-MS) were obtained using an Agilent 100 series MSD VL spectrometer. Gas Chromatography Mass spectra (GC/MS) were obtained using an Agilent technologies 6890N network GC system and equipped with Agilent Technologies 5975 inert XL mass selective detector.

Electronic Supplementary Material (ESI) for Dalton Transactions

Contents

Synthesis of the ligands

The ligand was synthesized according to the literature procedure.[1, 2] Ligand synthesis is presented schematically in the Scheme S1. Initially, 2-amino isobutyric acid was protected from reaction with phthalic anhydride. The acid chloride (**B**) of the corresponding amino acid (**A**) was obtained by reacting with $SOCl_2$ under reflux and the acid chloride was recrystallized from hexane. In dry THF, the purified acid chloride was used to react with aromatic diamine in presence of triethylamine to get a dipthalimide protected version of amidoamine ligand (**C**). Finally, the protected ligand was deprotected by using hydrazine hydrate to obtain the acyclic ligand (**1**) containing two free primary amine groups. All the ligands were characterized by ^{1}H and ^{13}C NMR, ESI-MS, FT-IR, and elemental analysis.



R_1, R_2 = H, H (**1a**); R_1, R_2 = Cl, Cl (**1b**);
R_1, R_2 = H, NO_2 (**1c**) R_1, R_2 = CH_3, CH_3 (**1d**)

R_1, R_2 = H, H (**C1**); R_1, R_2 = Cl, Cl (**CII**);
R_1, R_2 = H, NO_2 (**CIII**) R_1, R_2 = CH_3, CH_3 (**CIV**)

Scheme S1: Schematic representation of ligand synthesis.

2-Methyl-2-phthalimidopropanoic acid (A): Yield 90%. ^{1}H NMR (d_6-DMSO) 12.82 (s, 1 H, COOH), 7.81 (s, 4 H, ArH), 1.74 (s, 6 H, CH_3).

***Synthesis of 2-methyl-2-phthalimidopropanoyl chloride (B)*:** Yield 84%. ^{1}H NMR (d_6-DMSO) 7.83 (s, 4 H, ArH), 1.72 (s, 6 H, CH_3).

N,N'-(1,2-phenylene)bis(2-(1,3-dioxoisoindolin-2-yl)-2-methylpropanamide) (CI). Yield 85%. ^{1}H NMR (d_6 DMSO) 9.40 (s, 2 H), 7.82 (m, 4 H), 7.76 (m, 4 H), 7.53 (m, 2 H), 7.16 (m, 2 H), 1.74 (s, 12 H).

N,N'-(4,5-dichloro-1,2-phenylene)bis(2-(1,3-dioxoisoindolin-2-yl)-2-methylpropanamide) (CII): Yield 83%. %. ^{1}H NMR (d_6 DMSO) 9.45 (s, 2 H), 7.84 (m, 4 H), 7.83 (s, 2 H), 7.74 (m, 4 H), 1.70 (s, 12 H).

N,N'-(4-nitro-1,2-phenylene)bis(2-(1,3-dioxoisoindolin-2-yl)-2-methylpropanamide) (CIII): Yield 76%. %. ^{1}H NMR (d_6 DMSO) 9.40 (s, 2 H), 8.40 (m, 1 H), 8.12 (m, 1 H), 7.98 (m, 1 H), 7.87 (m, 4 H), 7.82 (m, 4 H), 1.70 (s, 12 H).

N,N'-(4,5-dimethyl-1,2-phenylene)bis(2-(1,3-dioxoisoindolin-2-yl)-2-methylpropanamide) (CIV): Yield 88%. %. ^{1}H NMR (d_6 DMSO) 9.46 (s, 2 H), 7.86 (m, 4 H), 7.84 (s, 2 H), 7.76 (m, 4 H), 2.65 (s, 6 H), 1.74 (s, 12 H).

2-Amino-N-[2-(2-amino-2-methyl-propionylamino)-phenyl]-2-methyl-propionamide (1a): Yield 93%. ^{1}H NMR (d_6 DMSO) 7.59 (m, 2 H), 7.16 (m, 2 H,), 4.70 (s (br), 4 H), 1.30 (s, 12 H). ^{13}C NMR (DMSO) 177.21 (2C, carbonyl), 131.4, 125.27, 124.54 (6C, aromatic), 55.37 (2C, sp^3 carbon), 29.15 (4C, methyl).

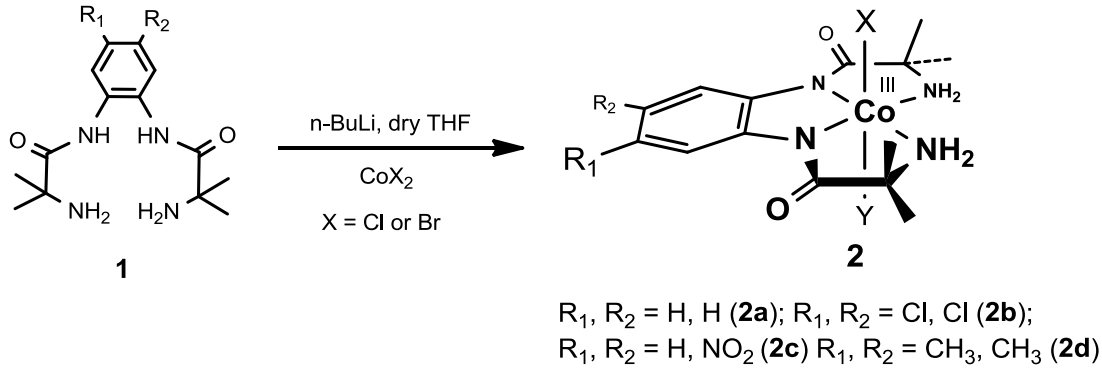
N,N'-(4,5-dichloro-1,2-phenylene)bis(2-amino-2-methylpropanamide) (1b): Yield 88%. ^{1}H NMR (d_6 DMSO) 7.94 (m, 2 H), 4.87 (s (br), 4 H), 1.30 (s, 12 H). ^{13}C NMR (DMSO) 177.53 (2C, carbonyl), 131.76, 126.45, 125.16 (6C, aromatic), 55.51 (2C, sp^3 carbon), 28.95 (4C, methyl).

N,N'-(4-nitro-1,2-phenylene)bis(2-amino-2-methylpropanamide) (1c): Yield 82%. ^{1}H NMR (d_6 DMSO) 8.55 (m, 1 H), 8.12 (m, 1 H,), 8.02 (m, 1 H,), 5.22 (s (br), 4 H), 1.35 (s, 12 H). ^{13}C NMR (DMSO) 177.56 (2C, carbonyl), 114.2 - 140.5 (6C, aromatic), 56.22 (2C, sp^3 carbon), 28.42 (4C, methyl).

N,N'-(4,5-dimethyl-1,2-phenylene)bis(2-amino-2-methylpropanamide) (1d): Yield 90%. ^{1}H NMR (d_6 DMSO) 7.35 (m, 2 H), 4.50 (s (br), 4 H), 2.18 (s, 6 H), 1.29 (s, 12 H). ^{13}C NMR (DMSO) 177.03 (2C, carbonyl), 133.04, 128.94, 125.48 (6C, aromatic), 55.31 (2C, sp^3 carbon), 29.17 (4C, methyl) 19.49 (2C, Ar-methyl).

General procedure for catalyst synthesis (2)

Ligand **1** (1 eq.) was dissolved in dry THF under N_2 and n-BuLi (2.1 eq. 1.6M in hexane) was added at 0 °C. Dry solid $CoCl_2$ or $CoBr_2$ (1 eq.) was added to the solution. The solution was warmed up to room temperature and stirred overnight to yield a green precipitate. Air was admitted through a drying tube and a purple precipitate was collected. The mixture was filtered through silica gel, and the purple compound was eluted with methanol. The solution was evaporated to dryness under reduced pressure, and the resultant solid was washed with small amount of dichloromethane yielding the product as a purple powder. All the cobalt complexes were prepared similarly.



Scheme S2: Schematic representation of metal complex synthesis.

Characterization of ligands

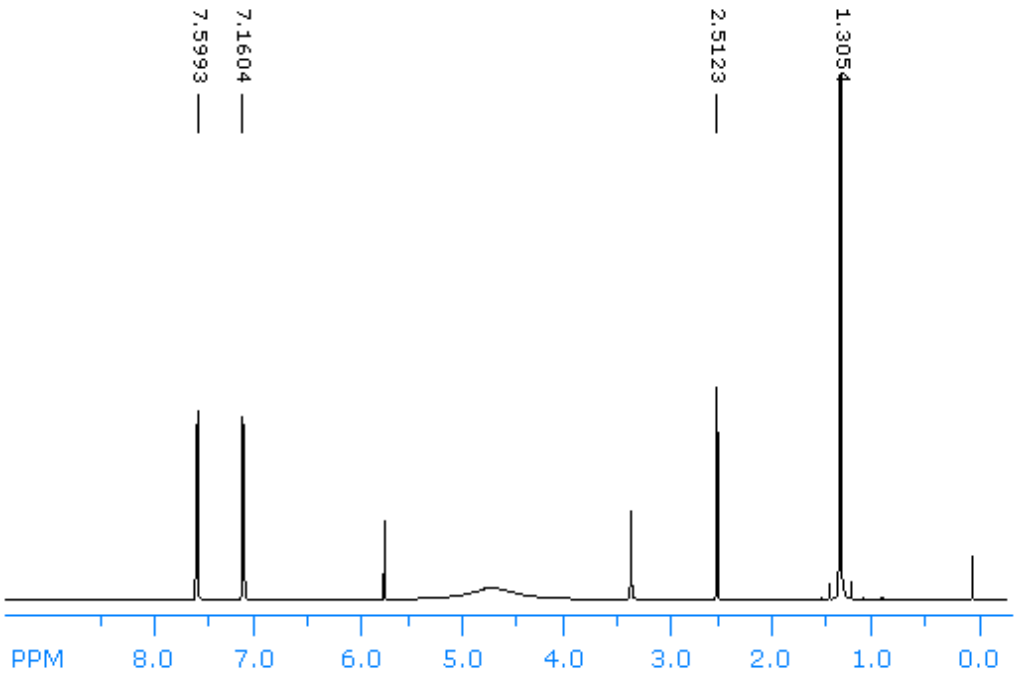


Figure S1: ^{1}H NMR of **1a.**

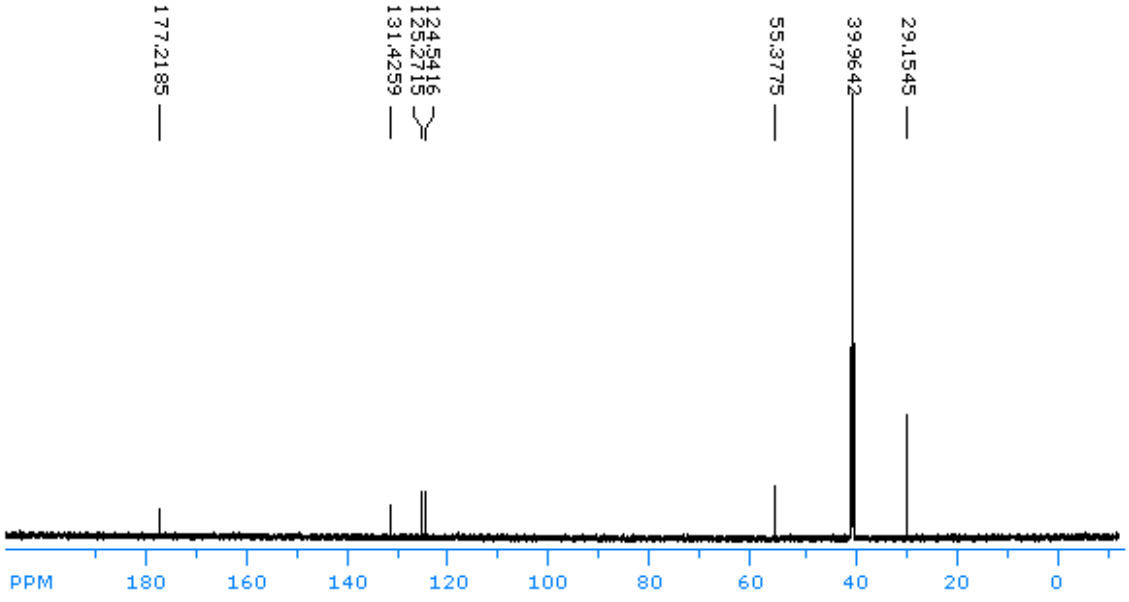


Figure S2: ^{13}C NMR of **1a.**

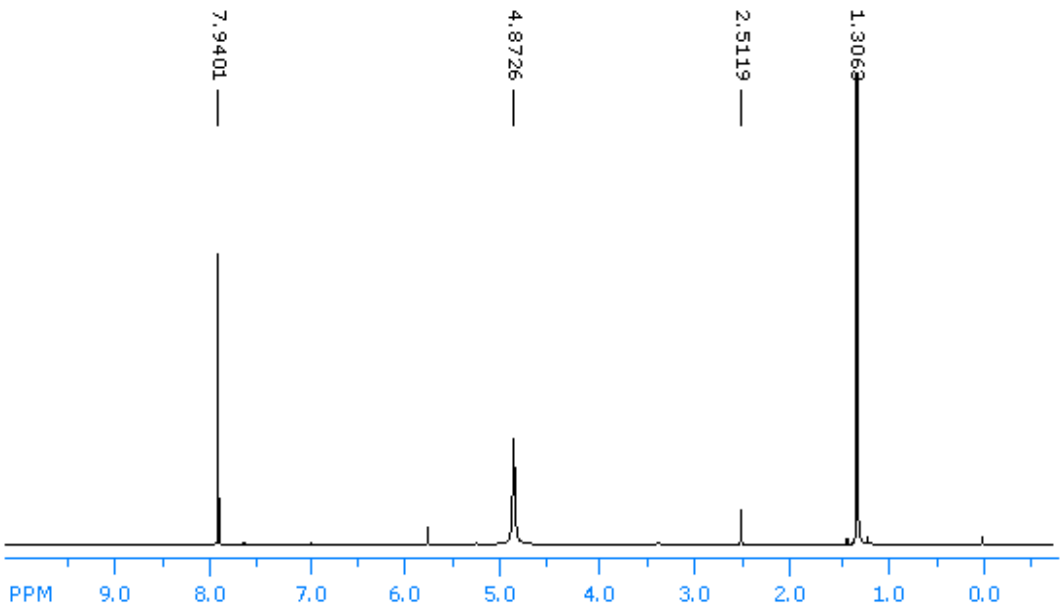


Figure S3: ^{1}H NMR of **1b.**

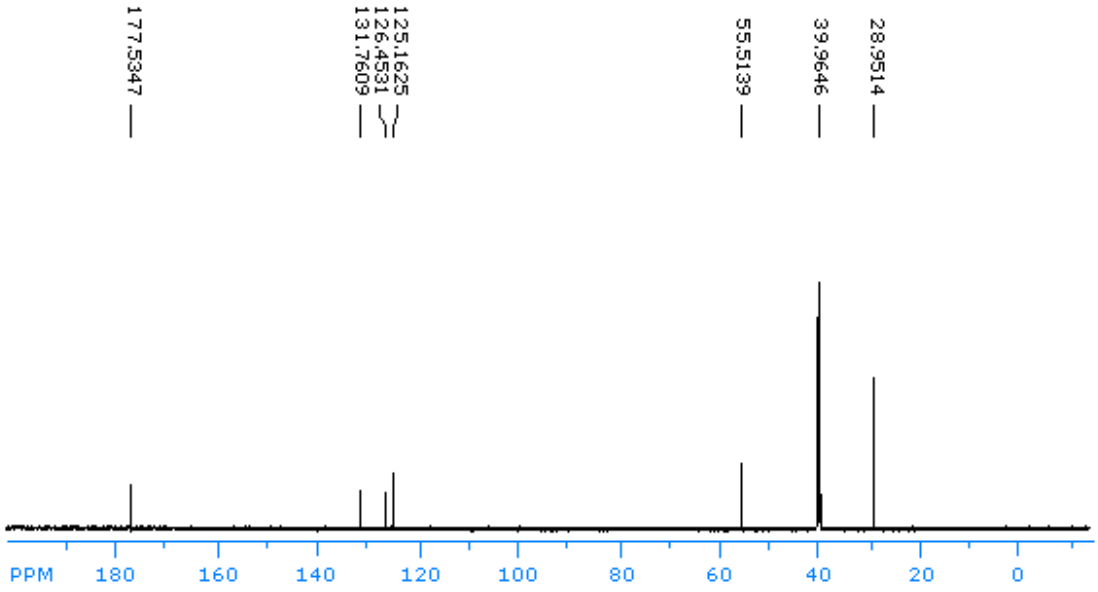


Figure S4: ^{13}C NMR of **1b.**

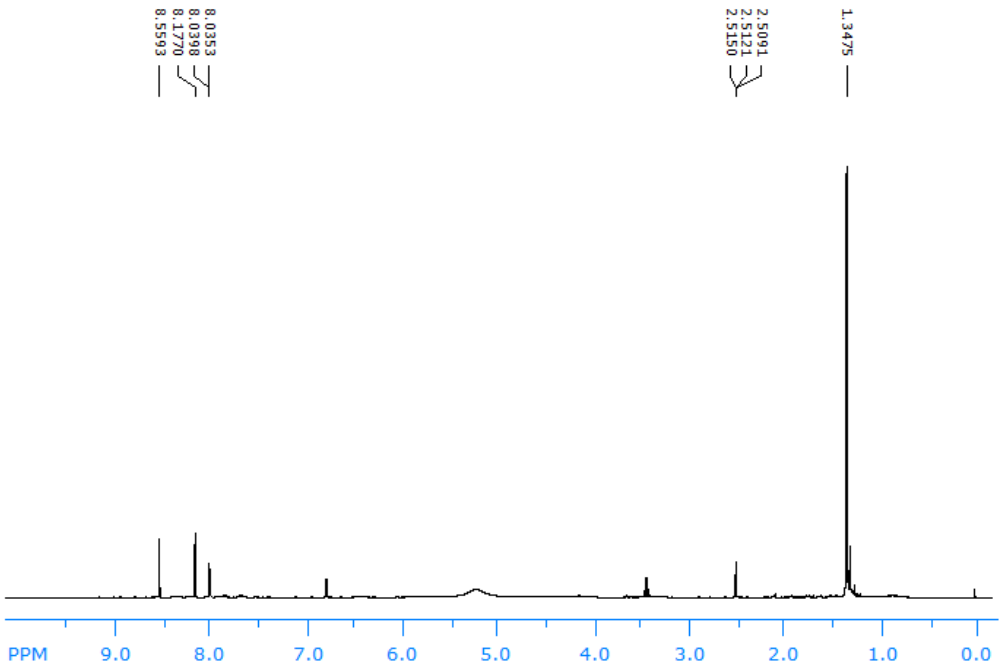


Figure S5: ^{1}H NMR of **1c.**

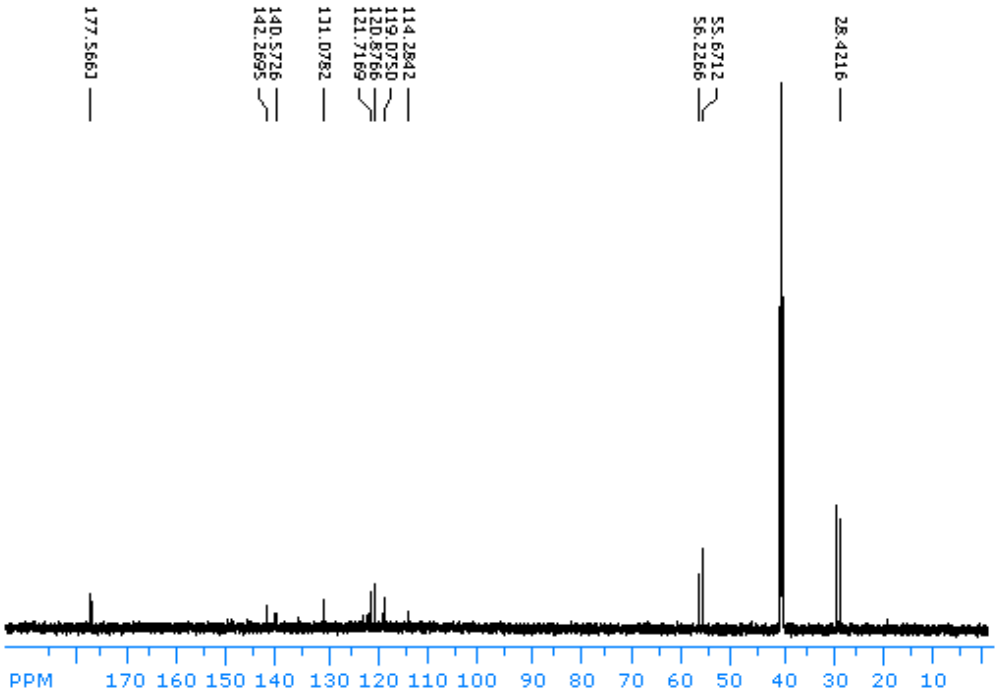


Figure S6: ^{13}C NMR of **1c.**

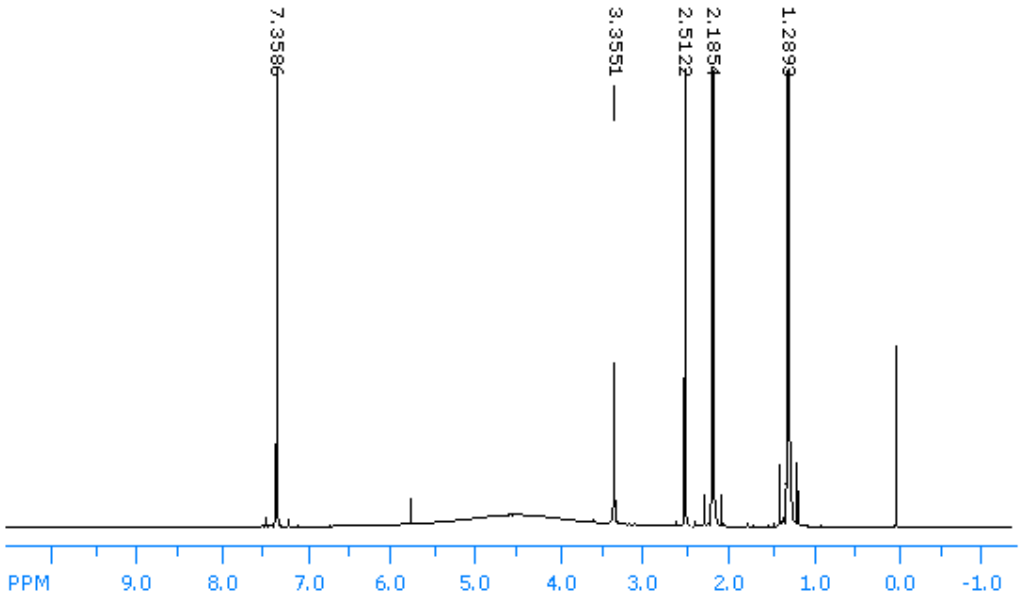


Figure S7: ^{1}H NMR of **1d.**

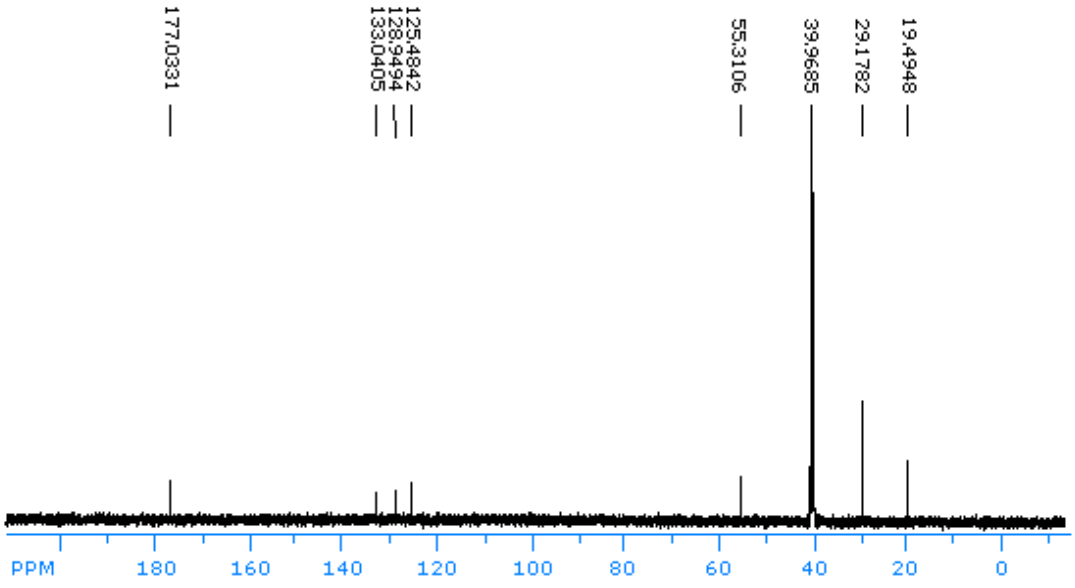


Figure S8: ^{13}C NMR of **1d.**

Characterization of metal complexes

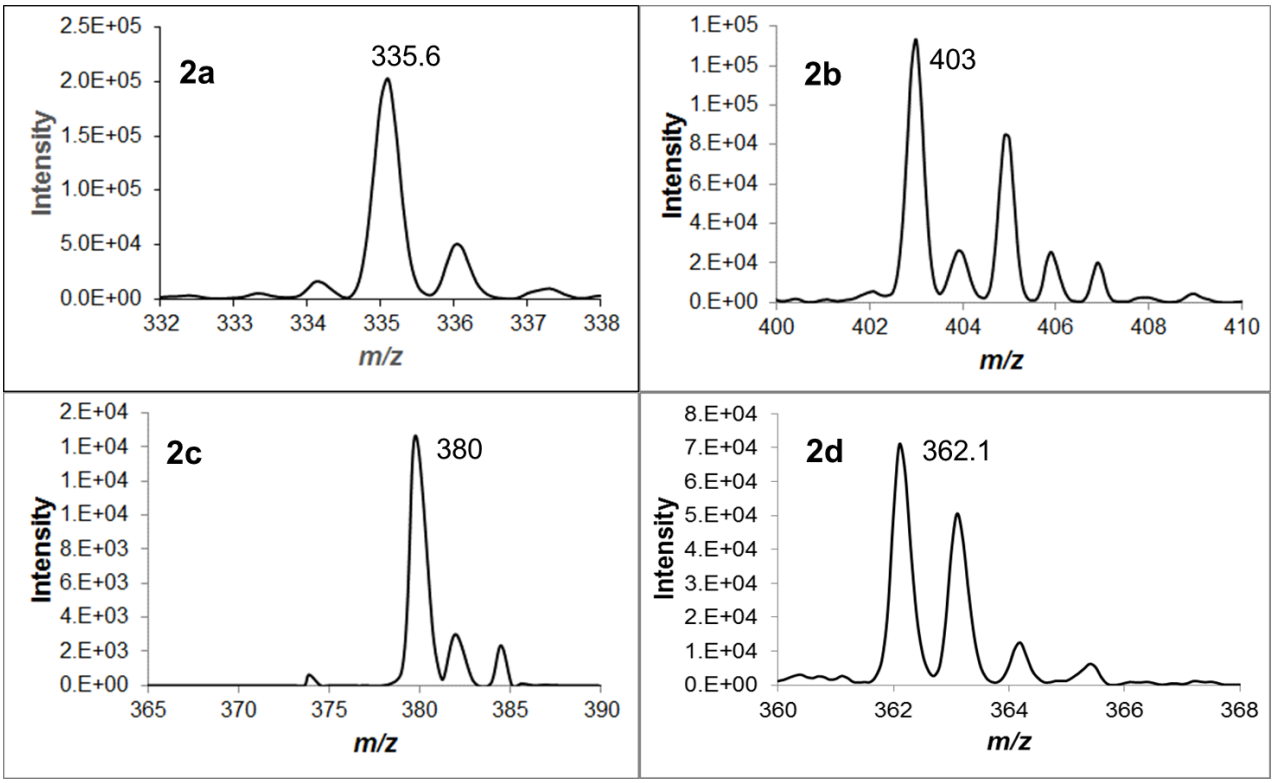


Figure S9: ESI-MS of Complex **2a-2d** (positive ion mode).

X-ray crystallographic data of 2a and 2b

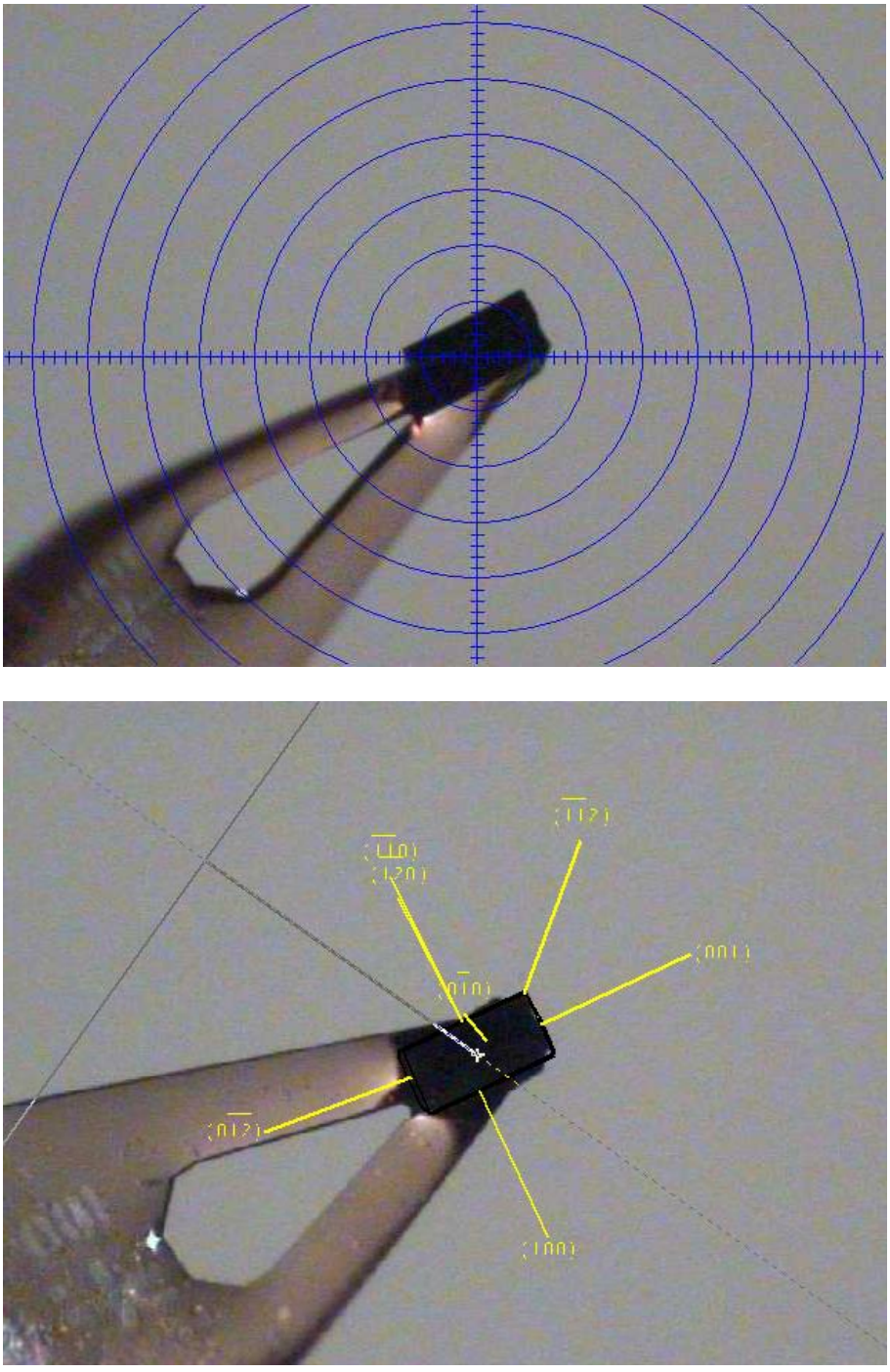


Figure S10: The video-microscope photographs of the single crystal of **2a** and its face-indexing.

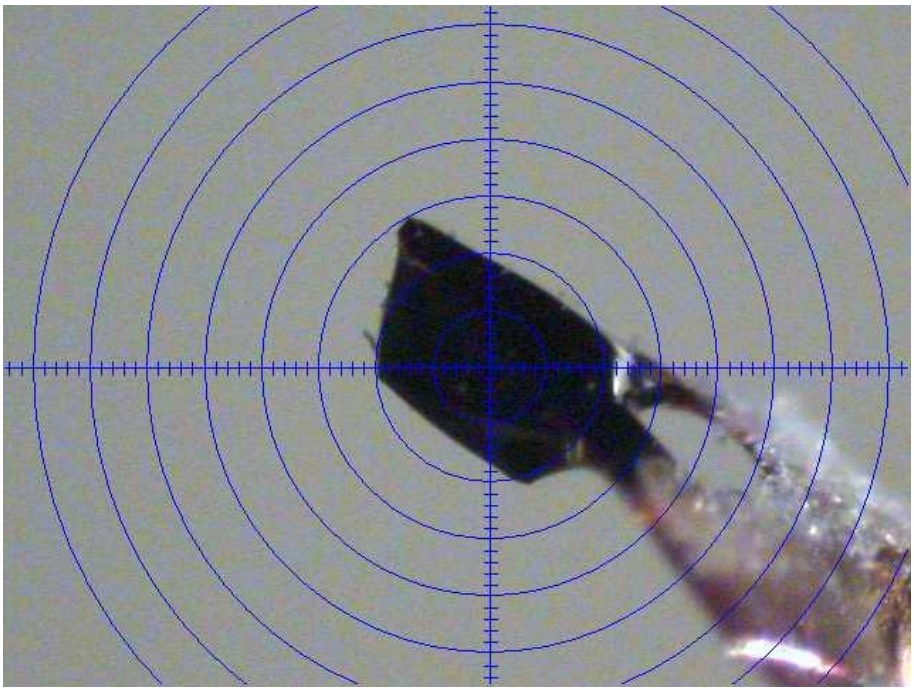


Figure S11: The video-microscope photographs of the single crystal of **2b** and its face-indexing.

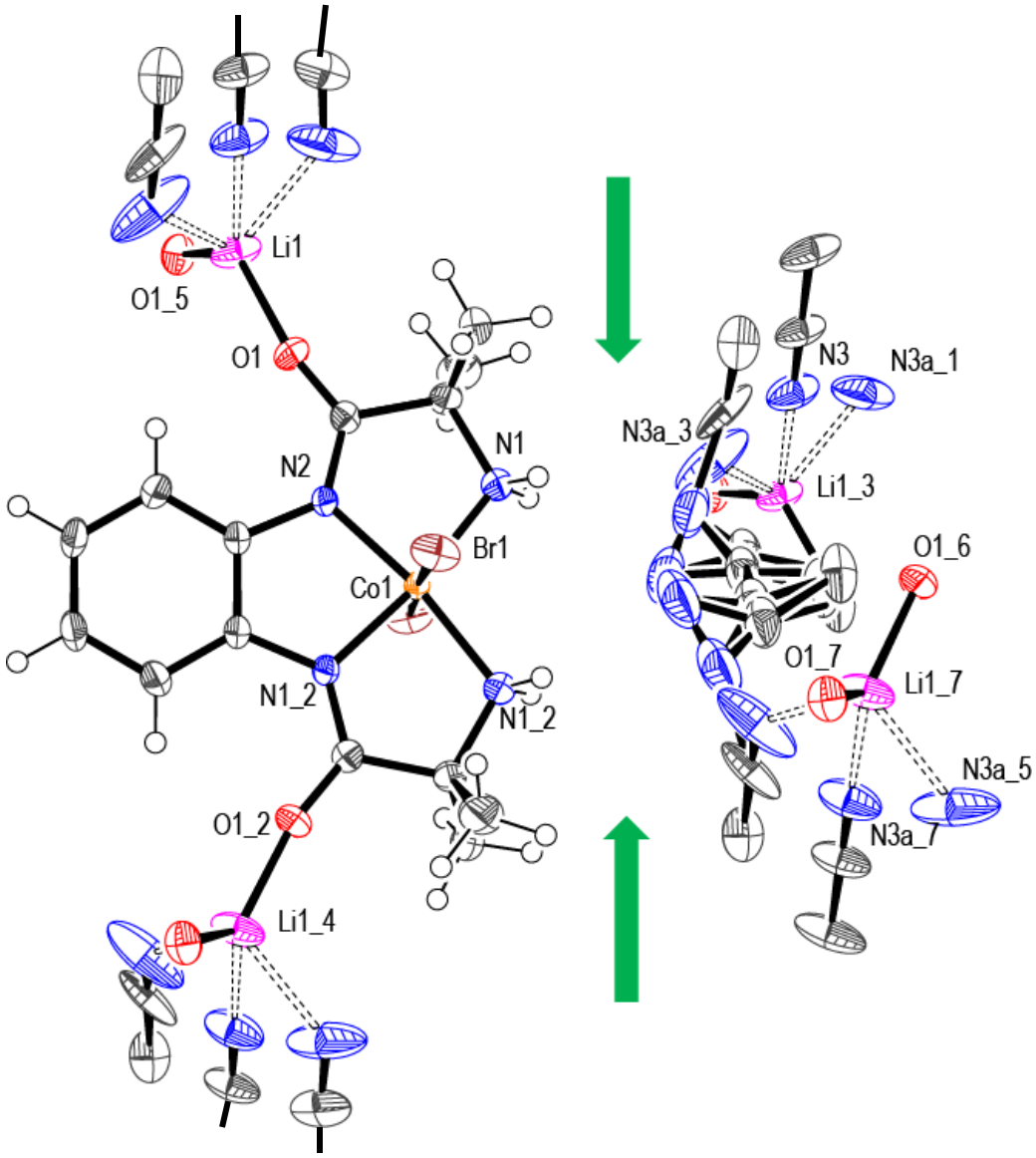


Figure S12: Top view of the $Li[CoL(Br)_2]$ complex **2a**. On the right: shown highly disordered cluster of acetonitrile molecules with N4 atoms of the solvent oriented towards NH_2-groups of the diimide ligand (displayed by arrows). On the left: seen partially shown CH_3CN molecules close to Li^+ counter-cations in the complex.

Symmetry transformations are:

#1 x, y, z;
#2 -x, -y, z+1/2,
#3 -x, y, -z+1/2;
#4 x, -y, -z
#5 x+1/2, y+1/2, z
#6 -x+1/2, -y+1/2, z+1/2
#7 -x+1/2, y+1/2, -z+1/2
#8 x+1/2, -y+1/2, -z

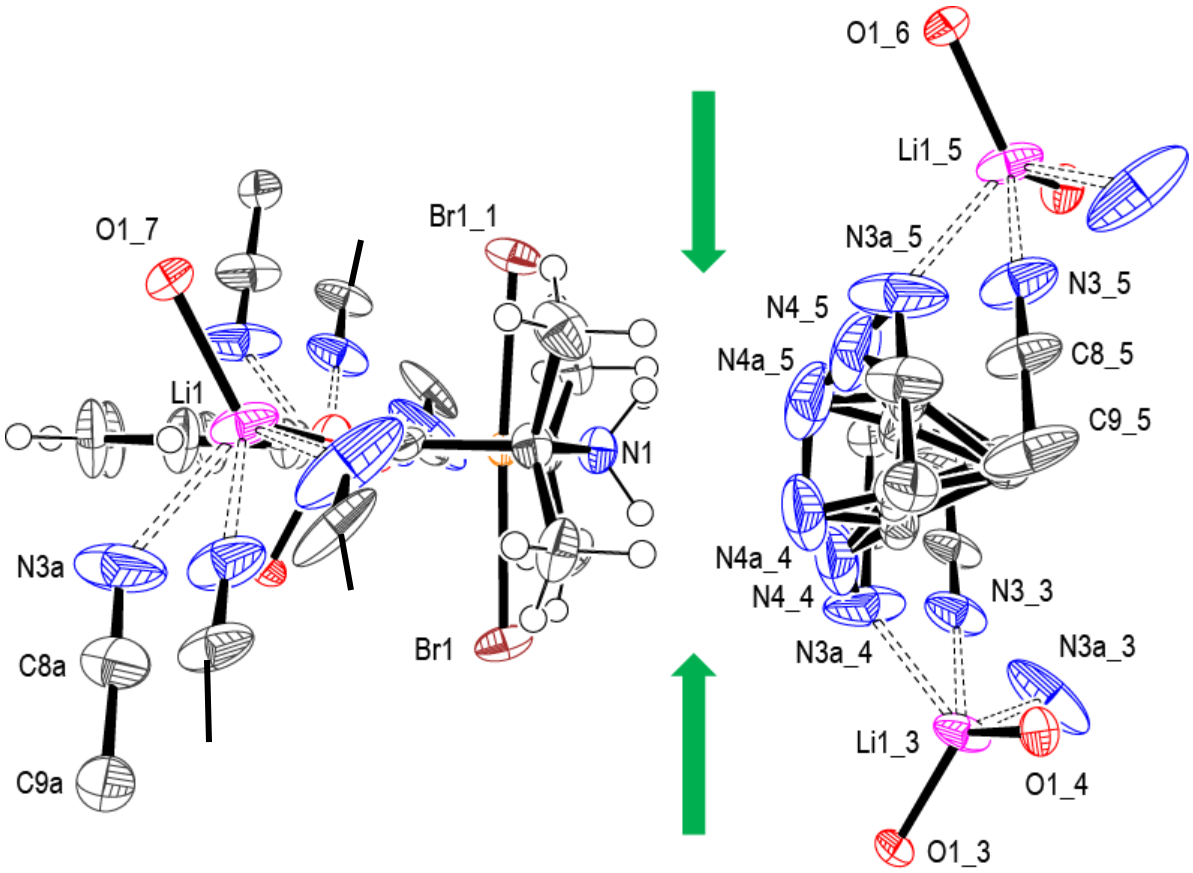
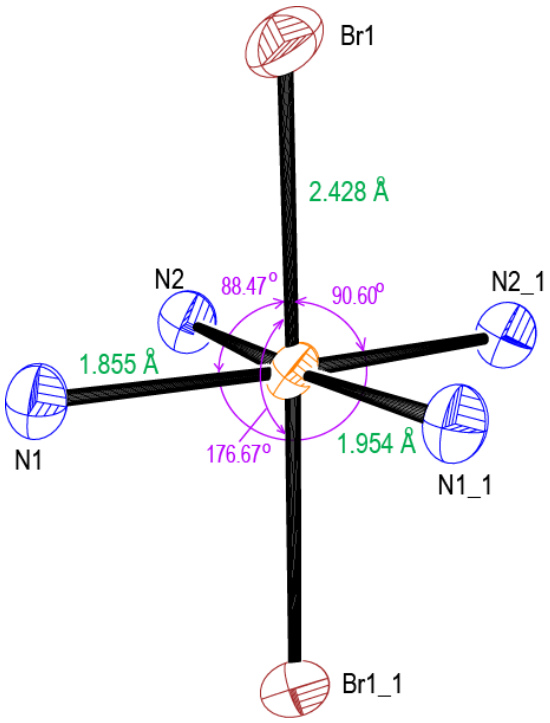


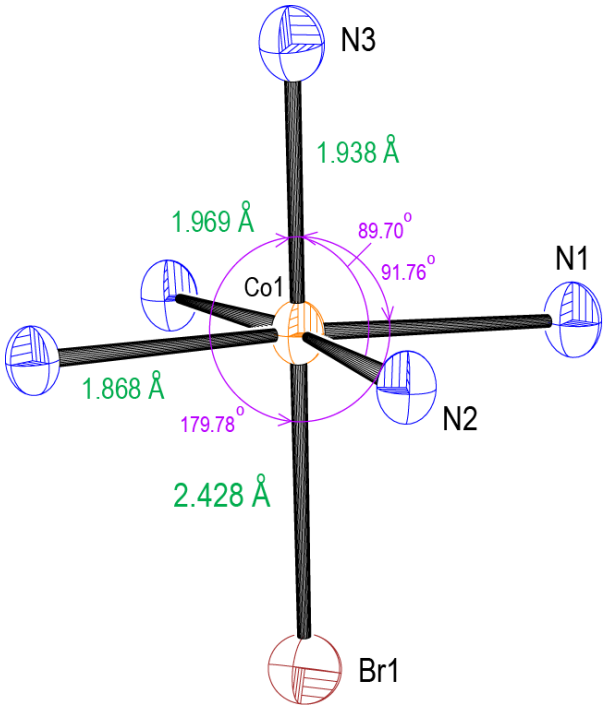
Figure S13: Side view of the Li[CoL(Br)$_2$] complex **2a**. On the right: shown highly disordered cluster of acetonitrile molecules with N4 atoms of the solvent oriented towards NH_2-groups of the diimide ligand (displayed by arrows). On the left: seen partially shown CH_3CN molecules close to Li^+ counter-cations in the complex.

Symmetry transformations are:

#1 x, y, z;
#2 -x, -y, z+1/2,
#3 -x, y, -z+1/2;
#4 x, -y, -z
#5 x+1/2, y+1/2, z
#6 -x+1/2, -y+1/2, z+1/2
#7 -x+1/2, y+1/2, -z+1/2
#8 x+1/2, -y+1/2, -z



2a



2b

Figure S14: Details of geometries of coordination polyhedrons of Co(III) centers in **2a** and **2b** complexes.

Crystal structure of complex **2a** has two kinds of disordered solvent (CH_3CN) molecules: one set of 3 molecules solvates Li^+ ion, while other 4 molecules occupy channels nearby that cation (see Figure S15 below). It should be especially noted that the main residue – Co(III) coordination compound – is perfectly ordered as can be judged from its ORTEP diagram. The only complicated disorder occurred with solvent that was in part a ligand bound to Li^+, and in part occupying channels in the structure.

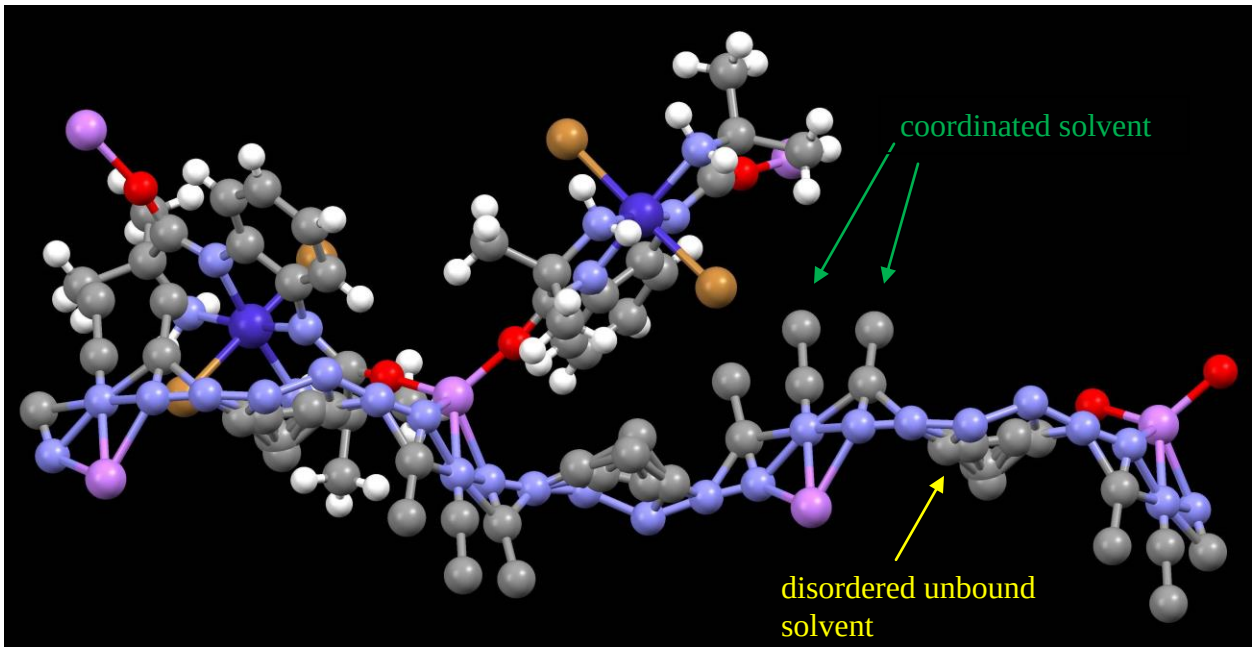


Figure S15: The ASU in the structure of **2a**: shown two kinds of disordered CH_3CN molecules. Green arrows indicate solvent coordinated to counter-cation, while yellow arrows indicate occluded into the channel "loose" solvent.

It was immediately obvious during the structure solution/refinement that there are molecules of disordered solvent. Moving slowly and stepwise in the process of structure refinement we made two models. Both models had restrains related only to the solvent molecules.

Thus, in one, simpler model, there were no H-atoms attached to all methyl groups of the solvent molecules, and we had only 3 of them bound to Li^+ cation. So, we had the following parameters:

R1 = 5.41%, GOF=1.028; 135 parameters and 11 DFIX and DANG constrain, but residual electron density was high (2.490 e).

Consequently, the second more complex and adequate model contained two groups of disordered solvent molecules. This model resulted in: R1 = 3.94%, GOF = 0.977; 190 parameters and 150 restrains (EADP, DFIX, SIMU, FLAT, DELU), with residual electron density only 0.469 e. Application of FLAT, SIMU and DELU restrains helped in refinement of the main residue core, while DFIX and EADP were applied for modeling of solvent molecules.

Both models led to publishable data, but the second one, more tedious, was selected for this paper.

Disordered solvent molecules could not be excluded (SQUEEZED out) from the data set since they provide absolutely crucial function for the crystal lattice formation. Thus, they form a "waving" chain along c-direction as shown in Figures S16 and S17 below.

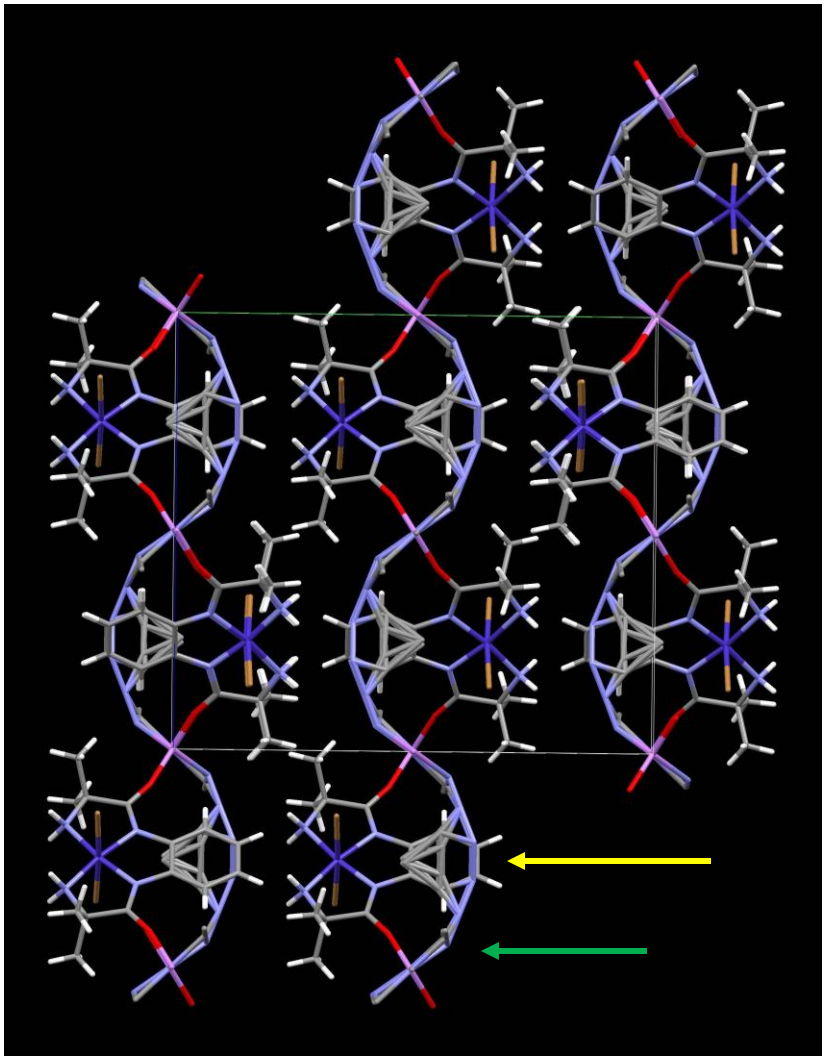


Figure S16: Packing diagram of the complex **2a**: Prospective view of several unit cells along *a*-direction. Arrows indicate disordered solvent molecules.

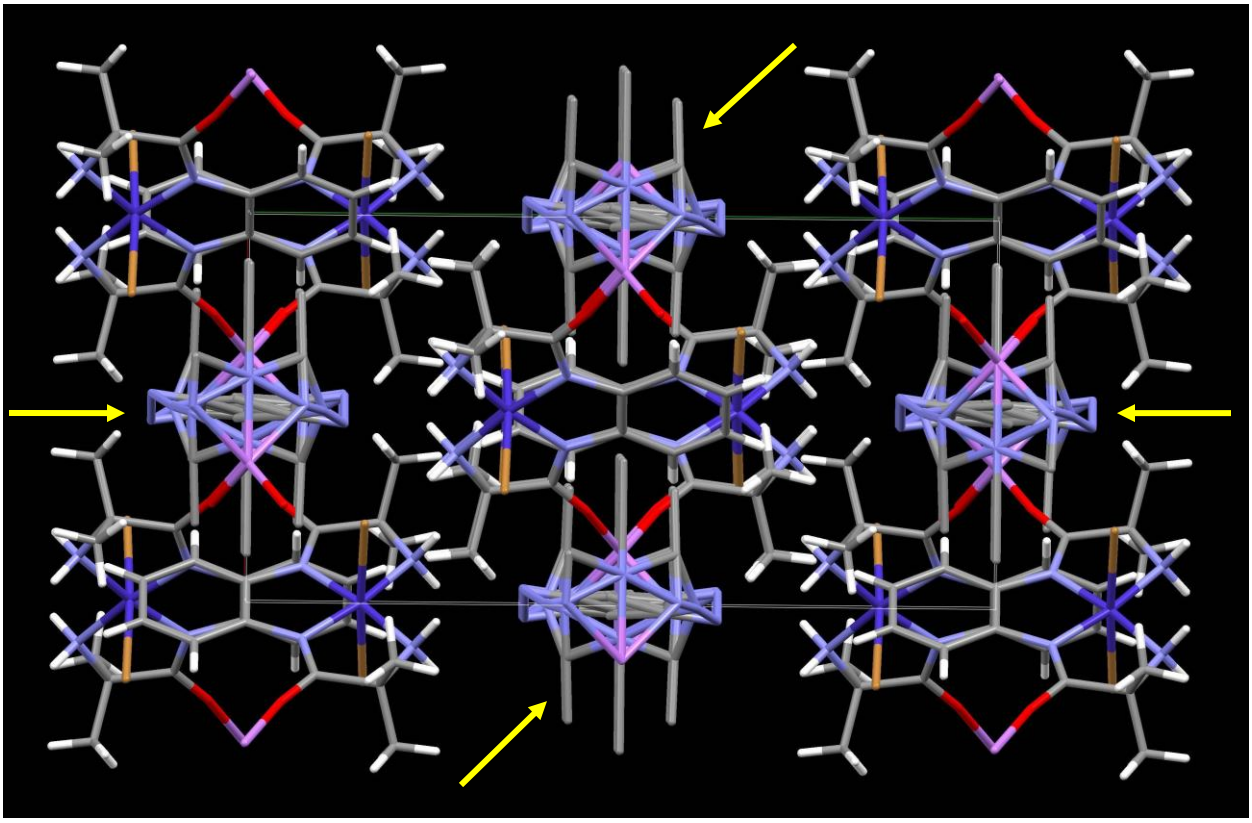


Figure S17: Packing diagram of the complex **2a**: Prospective view along *c*-direction. Arrows indicate channels filled with disordered CH_3CN molecules.

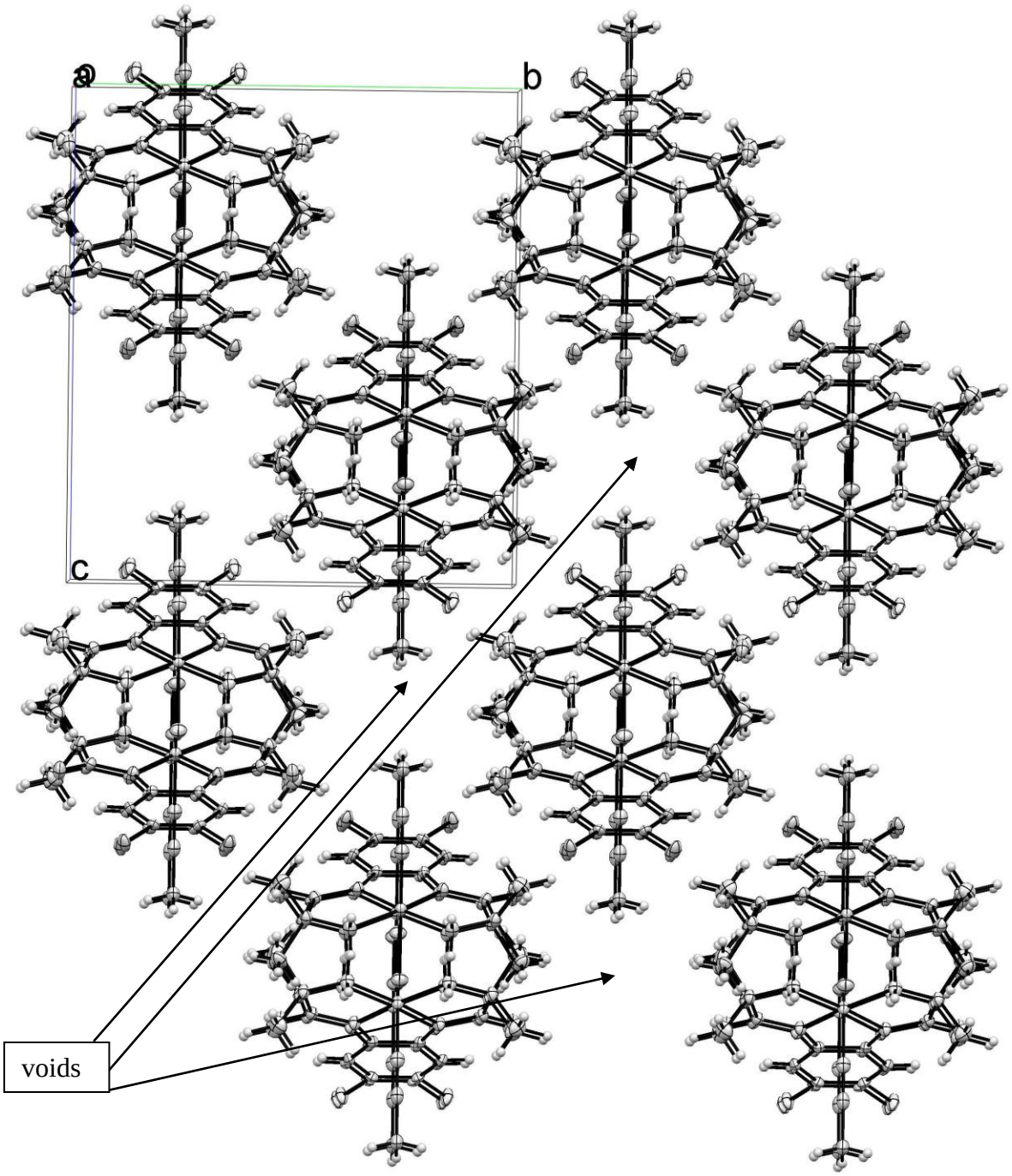


Figure S18: Prospective view of several unit cells along *a*-direction in the structure of **2b**. Shown two unit cells (in each dimension) to illustrate the presence of unoccupied by CH_3CN channels in the structure indicated by arrows.

Full crystal structure report for 2a

A dark black-brown prism-like specimen of $C_7H_8BrCoLiN_2O_{1.50}$ (main residue), approximate dimensions 0.100 mm x 0.130 mm x 0.250 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1456 frames were collected. The total exposure time was 8.09 hours. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 14354 reflections to a maximum θ angle of 27.16° (0.78 Å resolution), of which 2755 were independent (average redundancy 5.210, completeness = 99.6%, Rint = 6.65%, Rsig = 5.95%) and 2135 (77.50%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.0155(12) Å, b = 17.429(2) Å, c = 15.794(2) Å, volume = 2481.7(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 121 reflections above 20 $\sigma(I)$ with 5.065° < 2θ < 34.45°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.775. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3920 and 0.6654, respectively.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 2 2 2(1), #20, with Z = 8 for the formula unit, $C_7H_8BrCoLiN_2O_{1.50}$. The final anisotropic full-matrix least-squares refinement on F^2 with 190 variables converged at R1 = 3.94%, for the observed data and wR2 = 9.08% for all data. The goodness-of-fit was 0.985. The largest peak in the final difference electron density synthesis was 0.450 e-/$Å^3$ and the largest hole was -0.547 e-/$Å^3$ with an RMS deviation of 0.099 e-/$Å^3$. On the basis of the final model, the calculated density was 1.552 g/cm^3 and F(000), 1128 e-.

There are several molecules of disordered solvent (CH_3CN) in the structure that also have partial occupancy. Nevertheless, this disorder, complicated with partial occupancy of solvent molecules, was satisfactory modeled, but only for non-hydrogen atoms. We did not apply Platon SQUEEZ program in order not to alter experimental data.

Table S1: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Co(1)	0	11532(1)	-2500	17(1)
N(1)	1123(5)	12226(2)	-1766(2)	26(1)
C(1)	2071(4)	11794(3)	-1135(2)	25(1)
C(2)	1500(7)	11983(4)	-229(3)	43(2)
C(3)	3669(6)	11996(3)	-1241(4)	38(2)
C(4)	1857(4)	10932(3)	-1282(2)	20(1)
O(1)	2566(3)	10473(2)	-825(2)	30(1)
N(2)	924(3)	10751(2)	-1891(2)	19(1)
C(5)	516(3)	10005(3)	-2166(2)	27(1)
C(6)	1030(4)	9318(3)	-1834(3)	40(1)
C(7)	509(5)	8630(3)	-2172(3)	55(2)
Br(1)	2044(1)	11575(1)	-3500(1)	34(1)
Li(1)	3618(14)	10000	0	38(3)
N(3)	5846(11)	10000	0	52(4)
C(8)	7122(11)	10000	0	44(4)
C(9)	8732(11)	10000	0	60(6)
N(3A)	5113(14)	9250(10)	-584(10)	90(5)
C(8A)	6359(13)	9282(9)	-746(9)	60(4)
C(9A)	7963(15)	9310(7)	-896(8)	48(3)
N(4)	4980(130)	9000(60)	-1280(90)	76(4)
C(10)	4830(180)	9420(70)	-1850(80)	50(4)
C(11)	5000	10010(90)	-2500	48(5)
N(4A)	4644(15)	8720(6)	-2062(11)	76(4)
C(10A)	4880(20)	9370(7)	-2172(10)	50(4)
C(11A)	5240(30)	10154(6)	-2450(30)	48(5)

Table S2: Bond lengths [Å] and angles [°] for **2a**.

Bonds:	
Co(1)-N(2)#1	1.862(4)
Co(1)-N(2)	1.862(4)
Co(1)-N(1)	1.958(4)
Co(1)-N(1)#1	1.958(4)
Co(1)-Br(1)#1	2.4279(5)
Co(1)-Br(1)	2.4279(5)
N(1)-C(1)	1.514(6)
N(1)-H(1A)	0.9200
N(1)-H(1B)	0.9200
C(1)-C(3)	1.492(6)
C(1)-C(4)	1.533(7)
C(1)-C(2)	1.556(6)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-O(1)	1.253(5)
C(4)-N(2)	1.316(6)
O(1)-Li(1)	1.810(8)
N(2)-C(5)	1.419(6)
C(5)-C(6)	1.387(7)
C(5)-C(5)#1	1.407(9)
C(6)-C(7)	1.393(8)
C(6)-H(6)	0.9500
C(7)-C(7)#1	1.385(12)
C(7)-H(7)	0.9500
Li(1)-O(1)#2	1.810(7)
Li(1)-N(3)	2.009(17)
Li(1)-N(3A)#2	2.092(16)
Li(1)-N(3A)	2.092(16)
N(3)-C(8)	1.150(4)

C(8)-C(9)	1.451(4)
N(3A)-C(8A)	1.154(13)
C(8A)-C(9A)	1.466(13)
N(4)-C(10)	1.160(18)
C(10)-C(11)	1.468(18)
C(11)-C(10)#3	1.468(18)
N(4A)-C(10A)	1.167(13)
N(4A)-N(4A)#3	1.52(3)
N(4A)-C(10A)#3	1.711(19)
C(10A)-C(10A)#3	1.06(3)
C(10A)-C(11A)	1.469(14)
C(10A)-C(11A)#3	1.50(3)
C(10A)-N(4A)#3	1.711(19)
C(11A)-C(11A)#3	0.47(6)
C(11A)-C(10A)#3	1.50(3)

Angles:

N(2)#1-Co(1)-N(2)	86.2(2)
N(2)#1-Co(1)-N(1)	171.29(18)
N(2)-Co(1)-N(1)	85.11(17)
N(2)#1-Co(1)-N(1)#1	85.11(17)
N(2)-Co(1)-N(1)#1	171.29(18)
N(1)-Co(1)-N(1)#1	103.6(2)
N(2)#1-Co(1)-Br(1)#1	91.09(5)
N(2)-Co(1)-Br(1)#1	91.53(5)
N(1)-Co(1)-Br(1)#1	89.31(13)
N(1)#1-Co(1)-Br(1)#1	88.47(13)
N(2)#1-Co(1)-Br(1)	91.53(5)
N(2)-Co(1)-Br(1)	91.09(4)
N(1)-Co(1)-Br(1)	88.47(13)
N(1)#1-Co(1)-Br(1)	89.31(13)
Br(1)#1-Co(1)-Br(1)	176.42(5)
C(1)-N(1)-Co(1)	111.9(3)
C(1)-N(1)-H(1A)	109.2
Co(1)-N(1)-H(1A)	109.2
C(1)-N(1)-H(1B)	109.2

Co(1)-N(1)-H(1B)	109.2
H(1A)-N(1)-H(1B)	107.9
C(3)-C(1)-N(1)	110.7(4)
C(3)-C(1)-C(4)	109.6(3)
N(1)-C(1)-C(4)	108.5(4)
C(3)-C(1)-C(2)	111.9(4)
N(1)-C(1)-C(2)	108.2(4)
C(4)-C(1)-C(2)	107.8(3)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
O(1)-C(4)-N(2)	126.5(4)
O(1)-C(4)-C(1)	118.3(4)
N(2)-C(4)-C(1)	115.2(4)
C(4)-O(1)-Li(1)	166.6(3)
C(4)-N(2)-C(5)	127.5(4)
C(4)-N(2)-Co(1)	119.3(3)
C(5)-N(2)-Co(1)	113.3(3)
C(6)-C(5)-C(5)#1	120.3(3)
C(6)-C(5)-N(2)	126.1(4)
C(5)#1-C(5)-N(2)	113.6(3)
C(5)-C(6)-C(7)	119.1(5)
C(5)-C(6)-H(6)	120.5
C(7)-C(6)-H(6)	120.5
C(7)#1-C(7)-C(6)	120.7(3)
C(7)#1-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7

O(1)#2-Li(1)-O(1)	116.8(7)
O(1)#2-Li(1)-N(3)	121.6(4)
O(1)-Li(1)-N(3)	121.6(4)
O(1)#2-Li(1)-N(3A)#2	107.8(4)
O(1)-Li(1)-N(3A)#2	111.7(4)
N(3)-Li(1)-N(3A)#2	49.9(6)
O(1)#2-Li(1)-N(3A)	111.7(4)
O(1)-Li(1)-N(3A)	107.8(4)
N(3)-Li(1)-N(3A)	49.9(6)
N(3A)#2-Li(1)-N(3A)	99.8(12)
C(8)-N(3)-Li(1)	180.0
N(3)-C(8)-C(9)	180.0
C(8A)-N(3A)-Li(1)	134.0(17)
N(3A)-C(8A)-C(9A)	176.3(15)
N(4)-C(10)-C(11)	166(10)
C(10)-C(11)-C(10)#3	90(10)
C(10A)-N(4A)-N(4A)#3	77.7(11)
C(10A)-N(4A)-C(10A)#3	37.4(12)
N(4A)#3-N(4A)-C(10A)#3	41.8(6)
C(10A)#3-C(10A)-N(4A)	100.5(12)
C(10A)#3-C(10A)-C(11A)	70.6(18)
N(4A)-C(10A)-C(11A)	171(2)
C(10A)#3-C(10A)-C(11A)#3	67.7(16)
N(4A)-C(10A)-C(11A)#3	159(2)
C(11A)-C(10A)-C(11A)#3	18(2)
C(10A)#3-C(10A)-N(4A)#3	42.1(6)
N(4A)-C(10A)-N(4A)#3	60.5(14)
C(11A)-C(10A)-N(4A)#3	110.7(19)
C(11A)#3-C(10A)-N(4A)#3	109.9(18)
C(11A)#3-C(11A)-C(10A)	84(3)
C(11A)#3-C(11A)-C(10A)#3	77(4)
C(10A)-C(11A)-C(10A)#3	41.7(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z-1/2 #2 x,-y+2,-z #3 -x+1,y,-z-1/2

Table S3: Torsion angles [°] for **2a**.

N(2)#4-Co(1)-N(1)-C(1)	-1.3(11)
N(2)-Co(1)-N(1)-C(1)	-0.3(2)
N(1)#4-Co(1)-N(1)-C(1)	179.6(3)
Br(1)#4-Co(1)-N(1)-C(1)	91.3(2)
Br(1)-Co(1)-N(1)-C(1)	-91.5(2)
Co(1)-N(1)-C(1)-C(3)	120.9(4)
Co(1)-N(1)-C(1)-C(4)	0.6(3)
Co(1)-N(1)-C(1)-C(2)	-116.1(4)
C(3)-C(1)-C(4)-O(1)	58.2(3)
N(1)-C(1)-C(4)-O(1)	179.3(2)
C(2)-C(1)-C(4)-O(1)	-63.8(3)
C(3)-C(1)-C(4)-N(2)	-121.8(3)
N(1)-C(1)-C(4)-N(2)	-0.7(2)
C(2)-C(1)-C(4)-N(2)	116.2(3)
N(2)-C(4)-O(1)-Li(1)	-158.5(17)
C(1)-C(4)-O(1)-Li(1)	21.5(17)
O(1)-C(4)-N(2)-C(5)	-0.10(7)
C(1)-C(4)-N(2)-C(5)	179.89(5)
O(1)-C(4)-N(2)-Co(1)	-179.47(9)
C(1)-C(4)-N(2)-Co(1)	0.51(10)
N(2)#4-Co(1)-N(2)-C(4)	179.73(8)
N(1)-Co(1)-N(2)-C(4)	-0.13(13)
N(1)#4-Co(1)-N(2)-C(4)	-179.3(9)
Br(1)#4-Co(1)-N(2)-C(4)	-89.29(6)
Br(1)-Co(1)-N(2)-C(4)	88.26(6)
N(2)#4-Co(1)-N(2)-C(5)	0.27(5)
N(1)-Co(1)-N(2)-C(5)	-179.58(15)
N(1)#4-Co(1)-N(2)-C(5)	1.2(9)
Br(1)#4-Co(1)-N(2)-C(5)	91.25(8)
Br(1)-Co(1)-N(2)-C(5)	-91.19(8)
C(4)-N(2)-C(5)-C(6)	0.30(9)
Co(1)-N(2)-C(5)-C(6)	179.71(5)
C(4)-N(2)-C(5)-C(5)#4	179.84(5)
Co(1)-N(2)-C(5)-C(5)#4	-0.76(13)

C(5)#4-C(5)-C(6)-C(7)	-0.06(3)
N(2)-C(5)-C(6)-C(7)	179.45(9)
C(5)-C(6)-C(7)-C(7)#4	-0.04(3)
C(4)-O(1)-Li(1)-O(1)#2	89.4(16)
C(4)-O(1)-Li(1)-N(3)	-90.6(16)
C(4)-O(1)-Li(1)-N(3A)#2	-35(2)
C(4)-O(1)-Li(1)-N(3A)	-143.8(14)
O(1)#2-Li(1)-N(3)-C(8)	0.0
O(1)-Li(1)-N(3)-C(8)	0.0
N(3A)#2-Li(1)-N(3)-C(8)	0.0
N(3A)-Li(1)-N(3)-C(8)	0.0
Li(1)-N(3)-C(8)-C(9)	0.0
O(1)#2-Li(1)-N(3A)-C(8A)	-130.6(15)
O(1)-Li(1)-N(3A)-C(8A)	99.6(17)
N(3)-Li(1)-N(3A)-C(8A)	-17.0(14)
N(3A)#2-Li(1)-N(3A)-C(8A)	-17.0(14)
Li(1)-N(3A)-C(8A)-C(9A)	85(31)
N(4)-C(10)-C(11)-C(10)#5	113(67)
N(4A)#5-N(4A)-C(10A)-C(10A)#5	14(3)
N(4A)#5-N(4A)-C(10A)-C(11A)	10(15)
C(10A)#5-N(4A)-C(10A)-C(11A)	-4(13)
N(4A)#5-N(4A)-C(10A)-C(11A)#5	68(6)
C(10A)#5-N(4A)-C(10A)-C(11A)#5	54(5)
C(10A)#5-N(4A)-C(10A)-N(4A)#5	-14(3)
C(10A)#5-C(10A)-C(11A)-C(11A)#5	77(10)
N(4A)-C(10A)-C(11A)-C(11A)#5	81(16)
N(4A)#5-C(10A)-C(11A)-C(11A)#5	90(10)
N(4A)-C(10A)-C(11A)-C(10A)#5	4(13)
C(11A)#5-C(10A)-C(11A)-C(10A)#5	-77(10)
N(4A)#5-C(10A)-C(11A)-C(10A)#5	13.3(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z-1/2 #2 x,-y+2,-z #3 -x+1,y,-z-1/2

#4 -x,y,-z+1/2 #5 -x+1,y,-z+1/2

checkCIF report /PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

No syntax errors found.
Please wait while processing ....
Structure factor report

CIF dictionary
Interpreting this report

Datablock: I — 2a, NG_698_AGhosh_1

Bond precision: C-C = 0.0064 A Wavelength=0.71073

Cell: a=9.0155(12) b=17.429(2) c=15.794(2)
alpha=90 beta=90 gamma=90

Temperature: 120 K

	Calculated	Reported
Volume	2481.7(5)	2481.8(6)
Space group	C 2 2 21	C 2 2 21
Hall group	C 2c 2	C 2c2
Moiety formula	C16.95 H20 Br2 Co Li N5.47 O2, 0.44(C4 N2), 0.05(C3 N2)	?
Sum formula	C18.89 H20 Br2 Co Li N6.47 O2	C9.45 H10 Br Co0.50 Li0.50 N3.24 O
Mr	595.40	297.71
Dx,g cm-3	1.594	1.594
Z	4	8
Mu (mm-1)	3.938	3.938
F000	1178.6	1179.0
F000'	1178.13	
h,k,lmax	11,22,20	11,22,20
Nref	1563[2762]	2756
Tmin,Tmax	0.546,0.674	0.577,0.746
Tmin'	0.370	

Correction method= MULTI-SCAN

Data completeness= 1.76/1.00 Theta(max)= 27.160

R(reflections)= 0.0394(2136) wR2(reflections)= 0.0911(2756)

S = 0.989 Npar= 190

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT220_ALERT_2_B Large Non-Solvent N Ueq(max)/Ueq(min) ... 4.7 Ratio

Alert level C

CHEMW03_ALERT_2_C The ratio of given/expected molecular weight as calculated from the _atom_site* data lies outside the range 0.99 <> 1.01
From the CIF: _cell_formula_units_Z 8
From the CIF: _chemical_formula_weight 297.71
TEST: Calculate formula weight from _atom_site_*

atom	mass	num	sum
C	12.01	9.18	110.29
H	1.01	10.00	10.08
N	14.01	3.10	43.49
O	16.00	1.00	16.00
Co	58.93	0.50	29.47
Br	79.90	1.00	79.90
Li	6.94	0.50	3.47

Calculated formula weight 292.69

PLAT048_ALERT_1_C MoietyFormula Not Given ..... ?
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT213_ALERT_2_C Atom C8A has ADP max/min Ratio ..... 3.5 prola
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for Li1
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 2.2
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0064 Ang
PLAT420_ALERT_2_C D-H Without Acceptor N1 - H1A ... ?
PLAT420_ALERT_2_C D-H Without Acceptor N1 - H1B ... ?
PLAT910_ALERT_3_C Missing # of FCF Reflections Below Th(Min) 1
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 2

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the _chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C9.45 H10 Br1 Co0.5 Li0.5 N3.2
Atom count from the _atom_site data: C9.182 H10 Br1 Co0.5 Li0.5 N3.
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a symmetry error - see SYMMG tests
From the CIF: _cell_formula_units_Z 8
From the CIF: _chemical_formula_sum C9.45 H10 Br Co0.50 Li0.50 N3.24
TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	75.60	73.46	2.14
H	80.00	80.00	0.00
Br	8.00	8.00	0.00
Co	4.00	4.00	0.00
Li	4.00	4.00	0.00
N	25.92	24.84	1.08
O	8.00	8.00	0.00

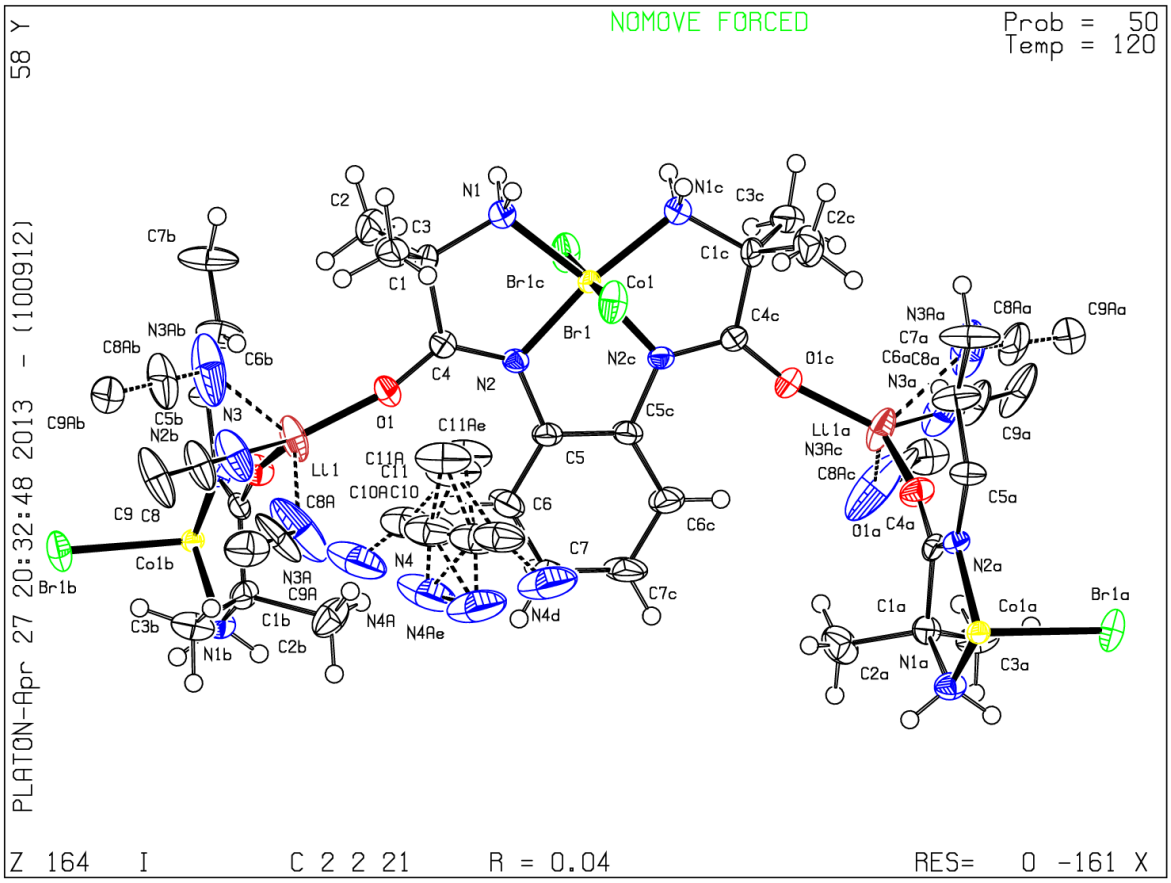
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 19
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 21
PLAT004_ALERT_5_G Info: Polymeric Structure Found with Dimension . 1
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms 2
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ..... 0.50 Ratio
PLAT093_ALERT_1_G No su's on H-positions, refinement reported as . mixed
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 18 Perc.
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 Perc.
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.19 Ratio
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 73
C10A -N4A -C10A 1.555 1.555 3.654 37.40 Deg.
And 4 other PLAT779 Alerts
More ...
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... !
PLAT850_ALERT_4_G Check Flack Parameter Exact Value 0.00 and su .. 0.02
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 150
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 2

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
11 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
22 **ALERT level G** = General information/check it is not something unexpected

6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
10 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
9 ALERT type 4 Improvement, methodology, query or suggestion
4 ALERT type 5 Informative message, check

PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock I - ellipsoid plot



Full crystal structure report for 2b

A metallic dark black-brown block-like specimen of $C_{16}H_{21}BrCl_2CoN_5O_2$, approximate dimensions 0.220 mm x 0.270 mm x 0.490 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1456 frames were collected. The total exposure time was 4.04 hours. The integration of the data using an orthorhombic unit cell yielded a total of 26557 reflections to a maximum θ angle of 29.13° (0.73 Å resolution), of which 2880 were independent (average redundancy 9.221, completeness = 99.6%, Rint = 3.01%, Rsig = 1.62%) and 2528 (87.78%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.2678(6) Å, b = 13.4525(8) Å, c = 14.9665(9) Å, volume = 2067.3(2) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5285 and 0.7620, respectively.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pnma, with Z = 4 for the formula unit, $C_{16}H_{21}BrCl_2CoN_5O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 173 variables converged at R1 = 3.83%, for the observed data and wR2 = 9.87% for all data. The goodness-of-fit was 1.091. The largest peak in the final difference electron density synthesis was 0.922 e-/$Å^3$ and the largest hole was -1.106 e-/$Å^3$ with an RMS deviation of 0.114 e-/$Å^3$. On the basis of the final model, the calculated density was 1.687 g/cm^3 and F(000), 1056 e-.

Table S4: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Complex **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Br(1)	4000(1)	2500	2992(1)	24(1)
C(1)	5421(3)	380(2)	1770(2)	18(1)
C(2)	6244(3)	-179(3)	1091(2)	28(1)
C(3)	5249(3)	-215(2)	2625(2)	26(1)
C(4)	4066(3)	584(2)	1350(2)	17(1)
C(5)	2731(2)	1971(2)	802(2)	14(1)
C(6)	1668(3)	1458(2)	456(2)	15(1)
C(7)	614(3)	1986(2)	114(2)	16(1)
C(8)	6174(4)	2500	-306(3)	22(1)
C(9)	6548(5)	2500	-1241(3)	23(1)
Cl(1)	-722(1)	1321(1)	-268(1)	23(1)
Co(1)	5041(1)	2500	1580(1)	16(1)
N(1)	6081(2)	1355(2)	1982(2)	20(1)
N(2)	3861(2)	1548(2)	1167(2)	16(1)
N(3)	5886(3)	2500	422(2)	22(1)
O(1)	3316(2)	-114(1)	1206(1)	24(1)

Table S5: Bond lengths [Å] and angles [°] for Complex **2b**

Bonds:	
Br(1)-Co(1)	2.3690(7)
C(1)-N(1)	1.509(4)
C(1)-C(3)	1.520(4)
C(1)-C(2)	1.520(4)
C(1)-C(4)	1.551(4)
C(2)-H(2A)	0.90(4)
C(2)-H(2B)	0.94(4)
C(2)-H(2C)	1.04(5)
C(3)-H(1A)	0.89(4)
C(3)-H(1B)	0.95(4)
C(3)-H(1C)	0.91(4)
C(4)-O(1)	1.233(3)
C(4)-N(2)	1.342(3)
C(5)-C(6)	1.392(3)
C(5)-N(2)	1.403(3)
C(5)-C(5)#1	1.422(5)
C(6)-C(7)	1.391(4)
C(6)-H(6)	0.82(4)
C(7)-C(7)#1	1.384(5)
C(7)-Cl(1)	1.735(3)
C(8)-N(3)	1.129(6)
C(8)-C(9)	1.452(6)
C(9)-H(9A)	0.84(5)
C(9)-H(9B)	0.93(10)
Co(1)-N(2)	1.868(2)
Co(1)-N(2)#1	1.868(2)
Co(1)-N(3)	1.937(4)
Co(1)-N(1)#1	1.969(2)
Co(1)-N(1)	1.969(2)
N(1)-H(1N1)	0.85(4)
N(1)-H(2N1)	0.80(5)

Angles:

N(1)-C(1)-C(3)	109.4(2)
N(1)-C(1)-C(2)	108.8(2)
C(3)-C(1)-C(2)	111.5(3)
N(1)-C(1)-C(4)	109.6(2)
C(3)-C(1)-C(4)	109.2(2)
C(2)-C(1)-C(4)	108.4(2)
C(1)-C(2)-H(2A)	112(2)
C(1)-C(2)-H(2B)	112(2)
H(2A)-C(2)-H(2B)	103(3)
C(1)-C(2)-H(2C)	110(2)
H(2A)-C(2)-H(2C)	112(3)
H(2B)-C(2)-H(2C)	107(3)
C(1)-C(3)-H(1A)	113(3)
C(1)-C(3)-H(1B)	112(2)
H(1A)-C(3)-H(1B)	107(3)
C(1)-C(3)-H(1C)	106(3)
H(1A)-C(3)-H(1C)	119(4)
H(1B)-C(3)-H(1C)	100(3)
O(1)-C(4)-N(2)	127.0(2)
O(1)-C(4)-C(1)	119.8(2)
N(2)-C(4)-C(1)	113.2(2)
C(6)-C(5)-N(2)	126.3(2)
C(6)-C(5)-C(5)#1	119.74(14)
N(2)-C(5)-C(5)#1	113.98(13)
C(7)-C(6)-C(5)	119.6(2)
C(7)-C(6)-H(6)	119(3)
C(5)-C(6)-H(6)	121(3)
C(7)#1-C(7)-C(6)	120.65(15)
C(7)#1-C(7)-Cl(1)	121.03(9)
C(6)-C(7)-Cl(1)	118.26(19)
N(3)-C(8)-C(9)	179.9(5)
C(8)-C(9)-H(9A)	108(3)
C(8)-C(9)-H(9B)	105(6)
H(9A)-C(9)-H(9B)	104(4)
N(2)-Co(1)-N(2)#1	86.58(13)

N(2)-Co(1)-N(3)	89.70(10)
N(2)#1-Co(1)-N(3)	89.70(10)
N(2)-Co(1)-N(1)#1	171.63(10)
N(2)#1-Co(1)-N(1)#1	85.19(10)
N(3)-Co(1)-N(1)#1	91.77(10)
N(2)-Co(1)-N(1)	85.19(10)
N(2)#1-Co(1)-N(1)	171.63(10)
N(3)-Co(1)-N(1)	91.77(10)
N(1)#1-Co(1)-N(1)	102.99(14)
N(2)-Co(1)-Br(1)	90.13(7)
N(2)#1-Co(1)-Br(1)	90.13(7)
N(3)-Co(1)-Br(1)	179.77(10)
N(1)#1-Co(1)-Br(1)	88.37(8)
N(1)-Co(1)-Br(1)	88.37(8)
C(1)-N(1)-Co(1)	111.84(16)
C(1)-N(1)-H(1N1)	112(2)
Co(1)-N(1)-H(1N1)	111(2)
C(1)-N(1)-H(2N1)	107(3)
Co(1)-N(1)-H(2N1)	109(3)
H(1N1)-N(1)-H(2N1)	106(4)
C(4)-N(2)-C(5)	127.0(2)
C(4)-N(2)-Co(1)	119.55(18)
C(5)-N(2)-Co(1)	112.72(16)
C(8)-N(3)-Co(1)	168.6(3)

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2, z

Table S6: Torsion angles [°] for Complex **2b**

N(1)-C(1)-C(4)-O(1)	-173.1(2)
C(3)-C(1)-C(4)-O(1)	-53.2(3)
C(2)-C(1)-C(4)-O(1)	68.4(3)
N(1)-C(1)-C(4)-N(2)	8.1(3)
C(3)-C(1)-C(4)-N(2)	127.9(3)
C(2)-C(1)-C(4)-N(2)	-110.4(3)
N(2)-C(5)-C(6)-C(7)	-179.9(2)
C(5)#1-C(5)-C(6)-C(7)	-0.2(3)
C(5)-C(6)-C(7)-C(7)#1	0.2(3)
C(5)-C(6)-C(7)-Cl(1)	-177.25(19)
C(3)-C(1)-N(1)-Co(1)	-123.5(2)
C(2)-C(1)-N(1)-Co(1)	114.5(2)
C(4)-C(1)-N(1)-Co(1)	-3.8(3)
N(2)-Co(1)-N(1)-C(1)	-0.50(19)
N(3)-Co(1)-N(1)-C(1)	-90.1(2)
N(1)#1-Co(1)-N(1)-C(1)	177.72(12)
Br(1)-Co(1)-N(1)-C(1)	89.77(18)
O(1)-C(4)-N(2)-C(5)	2.5(5)
C(1)-C(4)-N(2)-C(5)	-178.8(2)
O(1)-C(4)-N(2)-Co(1)	172.0(2)
C(1)-C(4)-N(2)-Co(1)	-9.3(3)
C(6)-C(5)-N(2)-C(4)	-8.8(4)
C(5)#1-C(5)-N(2)-C(4)	171.5(2)
C(6)-C(5)-N(2)-Co(1)	-178.8(2)
C(5)#1-C(5)-N(2)-Co(1)	1.43(17)
N(2)#1-Co(1)-N(2)-C(4)	-172.69(16)
N(3)-Co(1)-N(2)-C(4)	97.6(2)
N(1)-Co(1)-N(2)-C(4)	5.8(2)
Br(1)-Co(1)-N(2)-C(4)	-82.6(2)
N(2)#1-Co(1)-N(2)-C(5)	-1.8(2)
N(3)-Co(1)-N(2)-C(5)	-91.52(18)
N(1)-Co(1)-N(2)-C(5)	176.68(19)
Br(1)-Co(1)-N(2)-C(5)	88.33(16)
N(2)-Co(1)-N(3)-C(8)	43.29(7)

N(2)#1-Co(1)-N(3)-C(8)	-43.29(7)
N(1)#1-Co(1)-N(3)-C(8)	-128.47(7)
N(1)-Co(1)-N(3)-C(8)	128.47(7)

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2, z

checkCIF report /PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Structure factor report

Datablock: I — 2b, NG_690_AGhosh_3

```
Bond precision:      C-C = 0.0041 A              Wavelength=0.71073
Cell:          a=10.2678(6)    b=13.4525(8)    c=14.9665(9)
               alpha=90        beta=90         gamma=90
Temperature: 120 K
                    Calculated                      Reported
Volume              2067.3(2)                       2067.3(2)
Space group         P n m a                         Pnma
Hall group          -P 2ac 2n                       -P 2ac 2n
Moiety formula      C16 H21 Br Cl2 Co N5 O2         C16 H21 Br Cl2 Co N5 O2
Sum formula         C16 H21 Br Cl2 Co N5 O2         C16 H21 Br Cl2 Co N5 O2
Mr                  525.11                          525.12
Dx,g cm-3           1.687                           1.687
Z                   4                               4
Mu (mm-1)           3.043                           3.043
F000                1056.0                          1056.0
F000'               1057.72
h,k,lmax            14,18,20                        14,18,20
Nref                2891                            2880
Tmin,Tmax           0.388,0.512                     0.529,0.762
Tmin'               0.216
Correction method= NUMERICAL
Data completeness= 0.996        Theta(max)= 29.130
R(reflections)= 0.0383( 2528)      wR2(reflections)= 0.0987( 2880)
S = 1.091              Npar= 173
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT391_ALERT_3_B Deviating Methyl C3 H-C-H Bond Angle ..... 119 Deg.
PLAT391_ALERT_3_B Deviating Methyl C3 H-C-H Bond Angle ..... 100 Deg.
PLAT391_ALERT_3_B Deviating Methyl C9 H-C-H Bond Angle ..... 126 Deg.

Alert level C

PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.3 Ratio
PLAT350_ALERT_3_C Short C-H Bond (0.96A) C6 - H6 ... 0.82 Ang.
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 95 A**3
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 7

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 5.20
PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct. 9
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br1 -- Co1 .. 12.3 su
PLAT343_ALERT_2_G Check sp3 Angle Range in Main Residue for .. C9
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 2
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 4

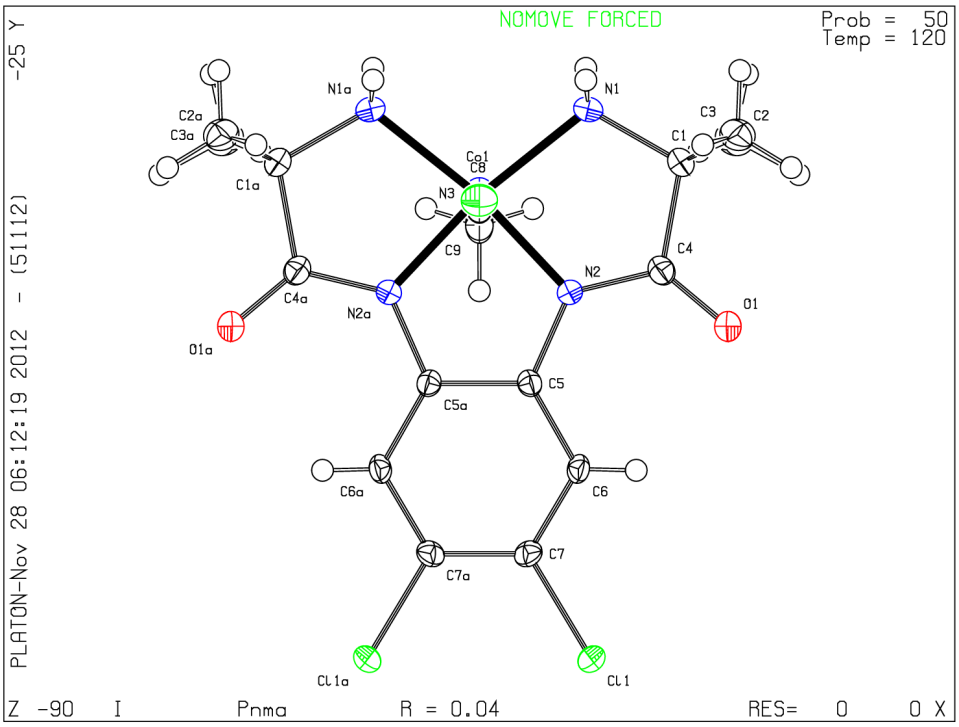
---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
3 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock I - ellipsoid plot



Product characterization

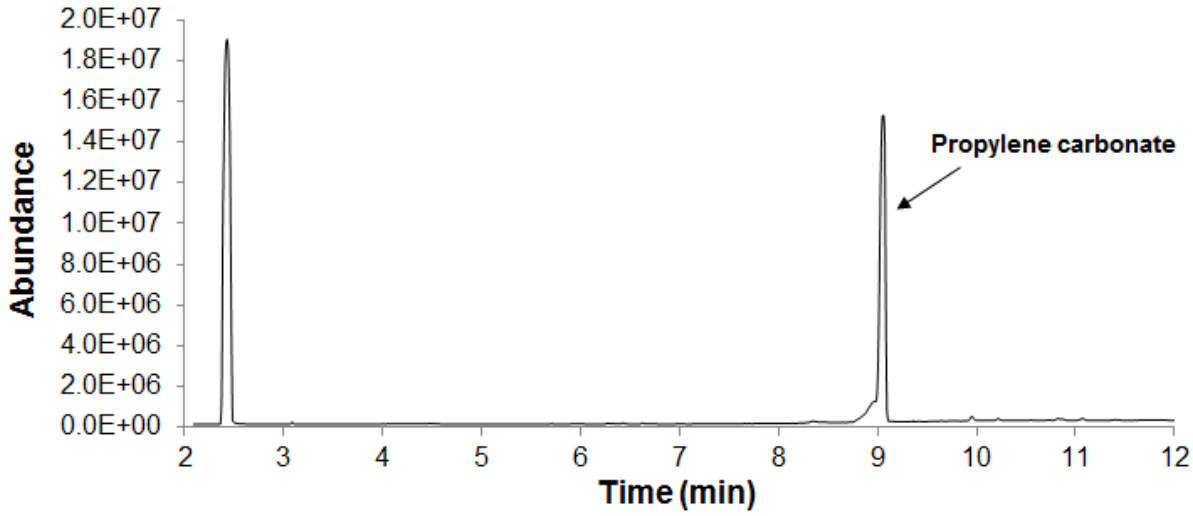


Figure S19: Gas chromatogram of the propylene carbonate.

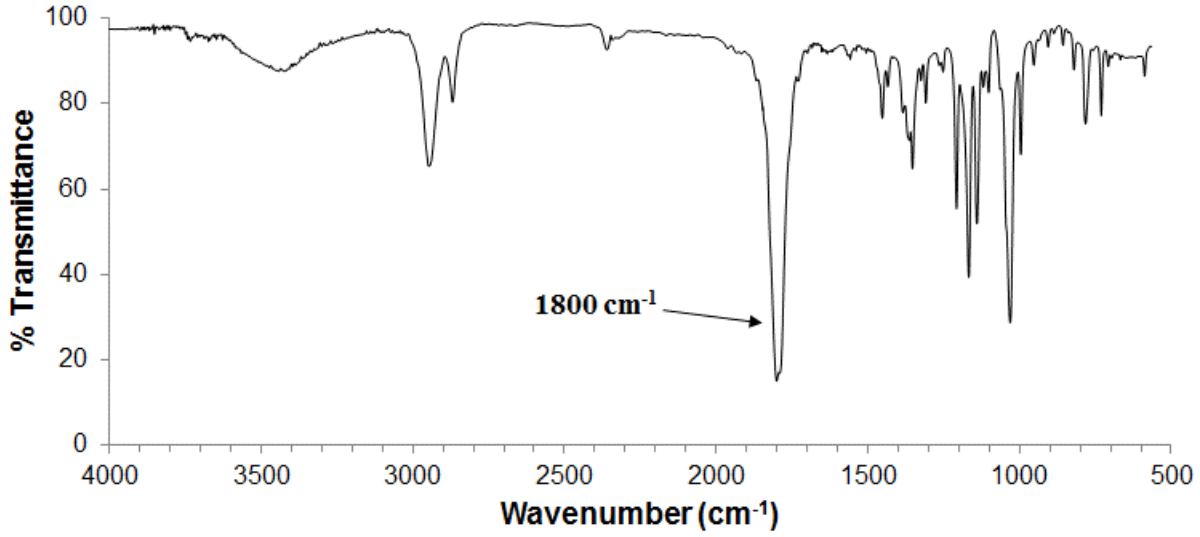


Figure S20: FT-IR Spectrum of cyclohexene carbonate.

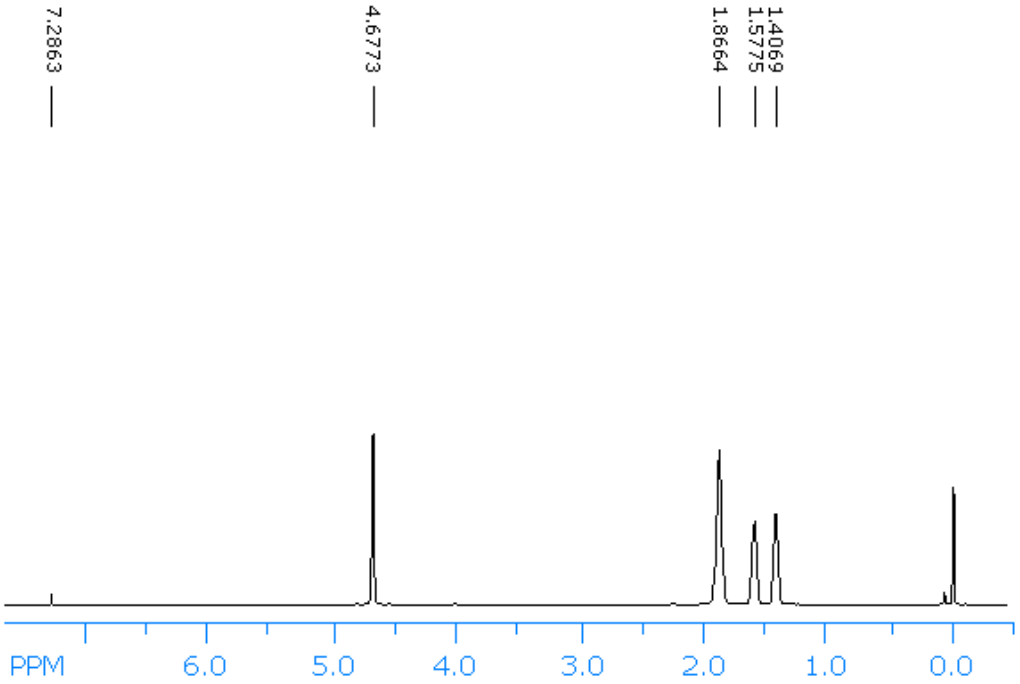


Figure S21: ^{1}H NMR spectra of cyclohexene carbonate.

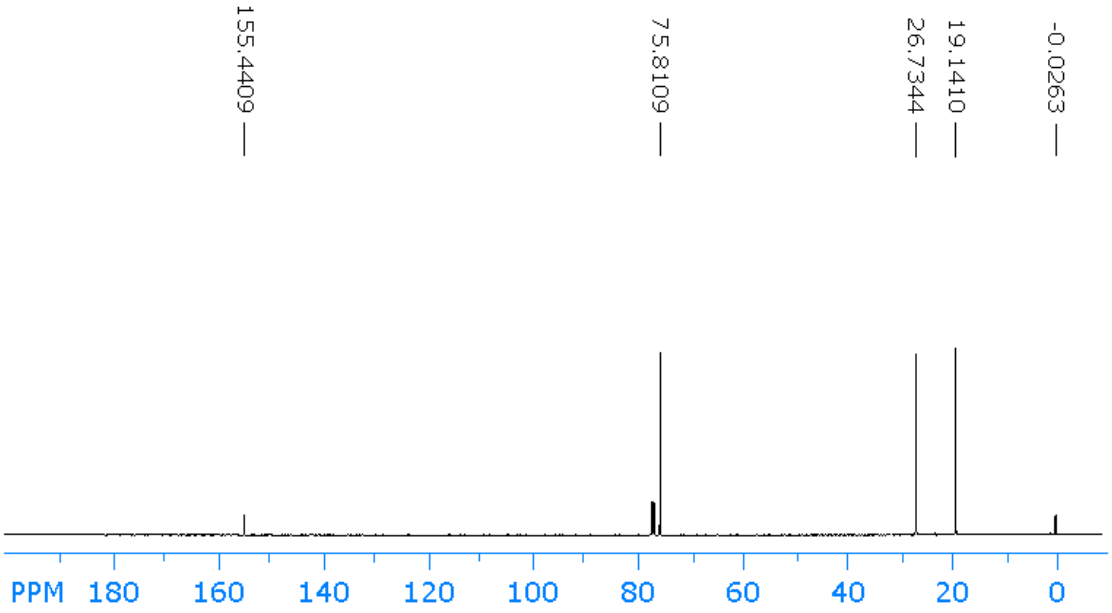


Figure S22: ^{13}C NMR spectra of cyclohexene carbonate.

Hammett plot

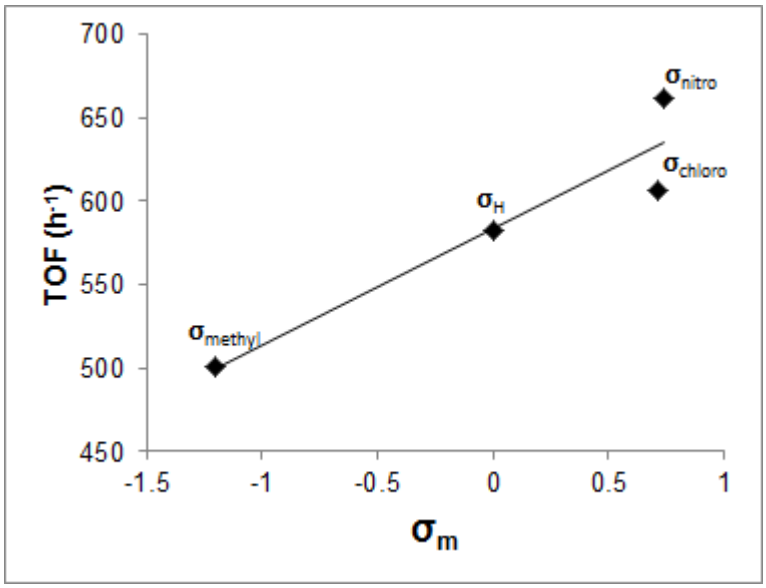


Figure S23: Hamett plot. Effect of substituents on TOF.

References

1. C. P. Horwitz and A. Ghosh, *US Patent, 7060818*, 2006.
2. A. Ghosh, P. Ramidi, S. Pulla, S. Z. Sullivan, S. L. Collom, Y. Gartia, P. Munshi, A. S. Biris, B. C. Noll and B. C. Berry, *Catal. Lett.*, 2010, **137**, 1-7.