ELECTRONIC SUPPLEMENTARY INFORMATION

Copper(II) cyclam based complexes for radiopharmaceutical applications: synthesis and structural analysis

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TABLE S1: Structure reference codes and bond distances for six coordinate copper(II) cyclam based structures deposited in the CSD (Distances 1 to 4 represent Cu-N_{macro} bond lengths).

Refcode	DIST1	DIST2	DIST3	DIST4	DIST5	DIST6
AKOBEH	2.039	2.039	2.056	2.056	2.590	2.590
BARWOH	2.007	2.007	2.011	2.011	2.475	2.475
BIJPUG	2.032	2.032	2.015	2.015	2.557	2.557
BIJTAQ	1.992	1.992	2.157	2.157	2.431	2.431
BIMSOG	2.015	2.015	2.037	2.037	2.534	2.534
BOJNUJ	1.996	1.996	2.051	2.051	2.667	2.667
BUTYUK	2.011	2.011	2.005	2.005	2.940	2.940
CEKHAB	2.047	2.047	2.077	2.077	2.565	2.565
CEMCAY	2.005	1.997	2.047	2.043	2.505	2.542
CESNUJ	2.029	2.029	1.981	1.981	2.602	2.602
CEVMAR	2.045	2.045	2.090	2.090	2.503	2.503
CEVMEV	2.031	2.031	2.050	2.050	2.623	2.623
CEVQAV	2.032	2.032	2.055	2.055	2.691	2.691
CEVQEZ	2.037	2.037	2.056	2.056	2.696	2.696
CEVQID	2.041	2.041	2.045	2.045	2.725	2.725
DEFJIH	2.032	2.032	2.035	2.035	2.815	2.815
DEFJIH01	2.028	2.028	2.037	2.037	2.763	2.763
DESHUE	2.008	2.010	2.098	2.054	2.603	2.535
DESQAT	2.077	2.077	2.109	2.109	2.317	2.317
DOHXON	2.010	2.010	2.015	2.015	2.515	2.515
ECIXIX	2.018	2.004	1.929	2.008	2.604	2.509
ECIXUJ	2.002	2.004	2.013	2.002	2.676	2.536
EFAQOR	2.152	2.152	2.048	2.048	2.356	2.356
FACFAR	2.025	2.025	2.009	2.009	2.602	2.602
FACFEV	1.948	1.948	2.008	2.008	2.835	2.835
FANFEF	2.027	2.027	2.022	2.022	2.524	2.524
FEQLOC	2.019	2.019	2.048	2.048	2.595	2.595
FERDIQ	2.025	2.025	2.020	2.020	2.548	2.548
FESKOE	2.012	2.012	2.018	2.018	2.546	2.546
FORMOO	2.428	2.368	1.994	2.015	2.004	2.005
GEWCEQ	2.014	2.014	2.095	2.095	2.262	2.262
GOXZIC	2.011	2.012	2.014	2.024	2.525	2.485
GUQTIV	2.043	2.043	2.038	2.038	2.582	2.582
GUTJUA	2.011	2.011	2.083	2.083	2.369	2.369
HANLUD	2.019	2.019	2.028	2.028	2.491	2.491
HANMEO	2.031	2.031	2.027	2.027	2.409	2.409
HANMEO	2.017	2.017	2.026	2.026	2.502	2.502
HAWJUK	2.017	2.017	2.019	2.019	2.514	2.514
HAWKAR	1.996	1.996	2.014	2.014	2.439	2.439
HAWKEV	2.020	2.020	2.027	2.027	2.535	2.535
HISHEW	2.009	2.051	1.968	2.107	2.551	2.705
IJAMUB	2.008	2.008	2.024	2.061	2.484	2.718
IPEYUX	2.016	2.016	1.922	1.922	2.454	2.454
IPEZAE	2.006	2.006	2.016	2.016	2.551	2.551
ITECIT	2.012	2.034	2.017	2.008	2.343	2.736
IVOMUB	2.010	2.010	2.044	2.044	3.072	3.072

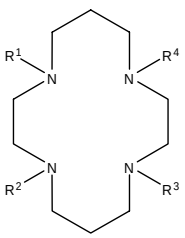
JABSUA	2.013	2.013	2.013	2.013	2.484	2.484
JUZZEJ	2.010	1.996	2.028	2.062	2.476	2.804
JUZZIN	2.027	2.072	2.021	2.071	2.566	2.732
JUZZOT	1.990	1.990	2.108	2.108	2.657	2.657
LESCOB	2.014	2.000	2.011	2.013	2.618	2.474
LEWCOF	2.069	2.069	2.094	2.094	2.309	2.309
LIWMAF	2.022	2.022	2.038	2.038	2.696	2.696
LIWMAG	2.080	2.080	2.081	2.081	2.721	2.721
LIZTET	2.025	2.025	2.032	2.032	2.338	2.338
LOJNED	2.029	2.004	2.024	2.023	2.925	2.994
LOTJOT	2.109	2.109	2.071	2.071	2.268	2.268
LOWCAB	2.016	2.027	2.014	2.010	2.660	2.506
LOYSAT	2.008	2.008	2.101	2.101	2.513	2.513
LUXMUM	2.035	2.036	2.029	2.031	2.371	2.370
MEFPAO	2.015	2.015	2.079	2.079	2.524	2.524
MUZTIK	1.999	2.012	2.018	1.950	2.485	2.517
NOPKUY	2.012	2.012	2.022	2.022	2.590	2.590
NUJVUJ	2.006	2.006	2.011	2.011	2.598	2.598
NUJVUJ01	2.012	2.012	2.017	2.017	2.536	2.536
NUVJET	2.002	2.008	2.040	2.103	2.932	2.809
OLIYEN	2.013	2.013	2.013	2.013	2.499	2.499
OMECEO	2.032	2.032	2.007	2.007	2.528	2.528
PELJEV	2.005	2.005	2.018	2.018	2.534	2.534
PIMFEW	2.056	2.056	2.108	2.108	2.248	2.248
POTPUJ	2.029	2.029	2.039	2.039	2.853	2.853
PTZDCU	2.016	2.016	2.024	2.024	2.567	2.567
QOJGOL	2.019	2.021	2.011	2.021	2.622	2.693
QUGKIM	2.030	2.030	2.039	2.039	2.505	2.505
RAJMIZ	2.066	2.066	2.029	2.029	2.434	2.434
RAXKIK	2.018	2.018	2.018	2.018	2.451	2.451
RAXKOQ	2.012	2.012	2.016	2.016	2.506	2.506
REYHEI	2.026	2.026	2.018	2.018	2.652	2.652
REYHIM	2.030	2.030	2.037	2.037	2.573	2.573
REYWEX	2.013	2.013	2.027	2.027	2.658	2.658
RILTOV	2.042	2.042	2.093	2.093	2.286	2.286
ROMWAR	2.011	2.011	2.016	2.016	2.569	2.569
ROMWEV	1.997	1.997	2.013	2.013	2.544	2.544
ROMWUL	2.005	2.005	2.003	2.003	2.867	2.867
SIBFIS	1.985	1.985	2.001	2.001	3.163	3.163
SUZTEM	2.045	2.045	2.085	2.085	2.314	2.314
TADWAX	2.020	2.026	2.014	2.013	2.489	2.497
TADWAX	2.013	2.019	2.012	2.013	2.505	2.414
TAWZIA	1.994	2.007	2.006	2.025	2.521	2.689
TEGPOK	2.023	2.023	2.016	2.016	2.953	2.953
TEHSUU	2.016	2.016	2.038	2.038	2.648	2.648
TEZREV	2.020	2.020	2.006	2.006	2.535	2.535
TEZRIZ	2.017	2.026	2.018	2.041	2.557	2.640
TUCQEN	2.020	2.020	2.027	2.027	3.193	3.193
UFOZIY	2.013	2.013	2.046	2.046	2.652	2.652
ULOLOW	2.008	2.008	2.042	2.042	2.551	2.551
VAHSIH	2.016	2.016	2.019	2.019	2.525	2.525
VOPSAU	2.096	2.096	2.070	2.070	2.368	2.368

WEQJEH	2.032	2.032	2.083	2.083	2.406	2.406
WOHYAT	2.015	2.012	2.013	1.995	2.526	2.600
WOHYEX	2.020	2.021	2.006	2.014	2.974	2.680
XETJAH	2.077	2.077	2.074	2.074	2.531	2.531
XODTOZ	1.975	1.975	2.025	2.025	2.535	2.535
XODTOZ	2.016	2.016	1.976	1.976	2.546	2.546
YEHPAC	2.018	2.018	2.018	2.018	2.842	2.842
YIWDOX	2.023	2.023	2.020	2.020	2.570	2.570
YIWFUF	2.018	2.018	2.013	2.013	2.448	2.448
YUMBUD	2.007	2.032	2.032	2.007	2.754	2.754
ZUGVAY	2.031	2.031	2.023	2.023	2.539	2.539
CAPVOF	2.021	2.021	2.053	2.053	2.592	2.592
DAPWOH	1.996	1.996	2.013	2.013	2.528	2.528
DAPXIC	2.024	2.024	2.016	2.022	2.585	2.287
DARPIW	2.030	2.030	2.012	2.012	2.582	2.582
DARPOC	2.029	2.029	2.016	2.016	2.681	2.681
DARPUI	2.026	2.023	2.020	2.023	2.414	2.752
TATFOK	2.026	2.015	2.019	2.081	3.069	2.312
YAVXID	2.028	2.028	2.030	2.030	2.398	2.398
JECDEB	2.069	2.021	2.035	2.115	2.294	2.351

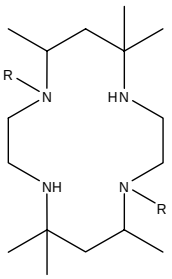
Compounds included:
all six coordinate copper(II) compounds incorporating the cyclam ring with the four nitrogens bound to the metal centre in an approximately square planar geometry.
C and N alkylated structures and ligands with N-pendant arms were also included.

Compounds excluded:
cryptands, configurationally restricted chelators and amide backbone structures.

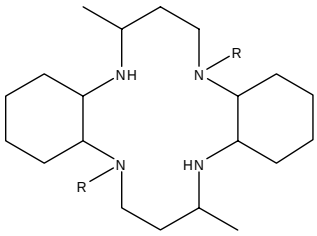
Figure S1: Formulae of some of the cyclam based chelators forming six-coordinate copper(II) compounds with structures deposited in the CSD.



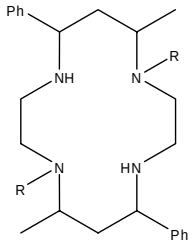
R selected from:
H
methyl
N,*N*-diethyl acetamide
methyl phosphonic acid
acetic acid
methylphenol
benzyl
methylpyridyl
ethylamine



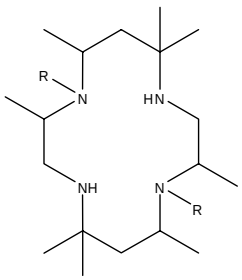
R equals:
H
ethanol
acetic acid



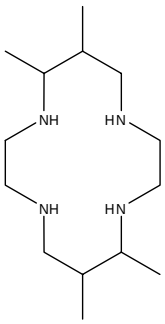
R equals:
H
acetamide
acetic acid
methylpyridyl

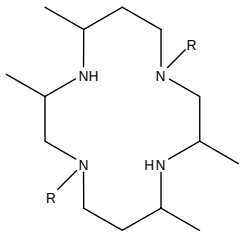


R equals:
H
acetic acid

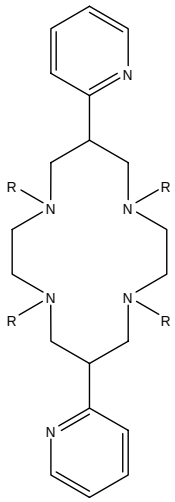


R equals:
H
ethanol

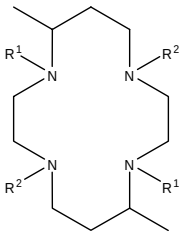




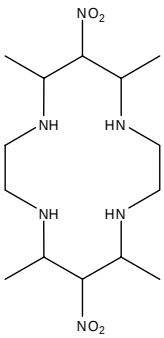
R equals:
H
methyl pyridyl

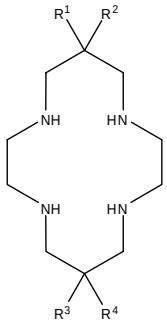


R equals:
H
methyl acetate
acetic acid



R selected from:
H
methyl
acetic acid

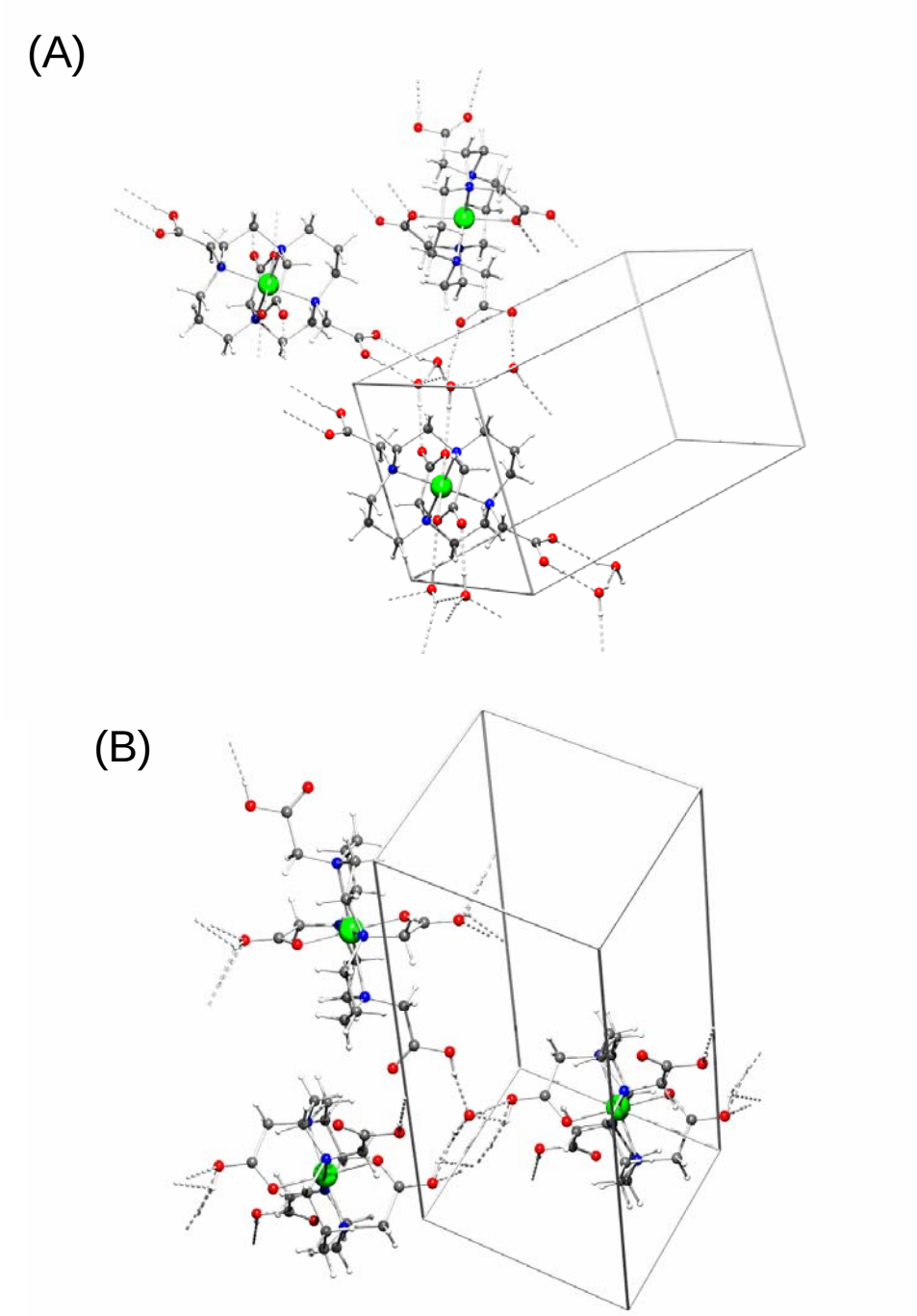




R selected from:
H
naphthyl
amine
formic acid
nitro
dimethylamine
nitrobenzyl

Not included in diagrams:
FORMOO
LOJNED
LIZTET
LOWCAB
NOPKUY
TADWAX
TAWZIA
TEZREV
TEZRIZ
WOHYAT
WOHYEX

Figure S2: The hydrogen bonded networks formed in the X-ray structures of the two CuH_2**TETA** complexes.



A linked network of hydrogen bonded species exists involving both the water molecules of crystallisation and the uncoordinated pendant arms, see Fig. S2. Structure (A) has four water molecules present for every complete copper macrocyclic unit (two waters per asymmetric unit). These waters H-bond to the coordinated and free carboxyl groups to form both an infinite three dimensional network and an infinite one dimensional chain within the structure. The D-H….A distances are in the range 2.587(2) to 2.973(2) Å with the shortest between a carboxyl group and a water molecule and the longest a bifurcated bond. Structure (B) has two water molecules present for every copper macrocyclic unit and also shows an infinite three dimensional H-bonded framework involving the carboxyl groups and the water molecules. This is composed of closed H-bonded rings rather than one dimensional chains. The D-H….A distances are in the range 2.628(2) Å to 2.905(2) Å. Linear and bifurcated H-bonds are present in both structures.

Figure S3: Histogram representing the Cu-L distances of non-macrocyclic trans donor groups from six coordinate copper(II) cyclam type X-ray structures deposited in the CSD (see above)