

the Chemical Database Service

NEWSLETTER

Autumn 2009

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Welcome

Welcome to the Autumn 2009 Newsletter of the Chemical Database Service (CDS)

See inside for details of the current state of the Service and what has changed over the past 6 months.

Latest News

Statement of Need and Mid-Range Facility Review

Thank you to all those users who added their name to our iPetition. The outcome of the review was that CDS was **viewed very highly** and will be a **priority for EPSRC support**.

More details on page 2

Login/Password/Registration

A number of changes have been made.

More details on pages 2 and 3.

CrystalWeb

CrystalWeb hit page now has links to **ChemSpider** (using InChI codes).

More details on page 5.

Accelrys and ISIS Databases

CDS are looking into the possibility of making the Accelrys and ISIS (now Symyx) databases available again

More details on page 7.



Science & Technology
Facilities Council



Links used in Newsletters can be found at:- <http://cds.dl.ac.uk/letterlinks>

Crystallography Databases

Thermophysical Database

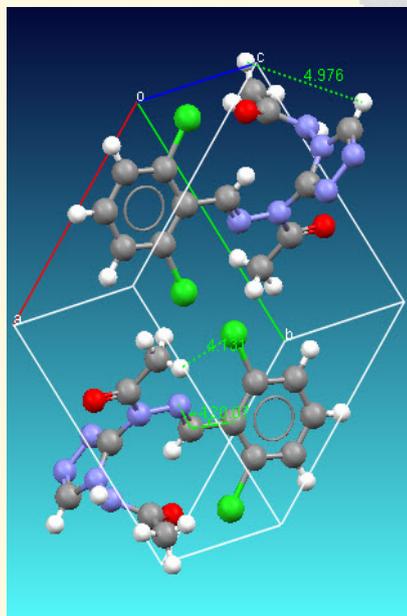
Spectroscopy Databases



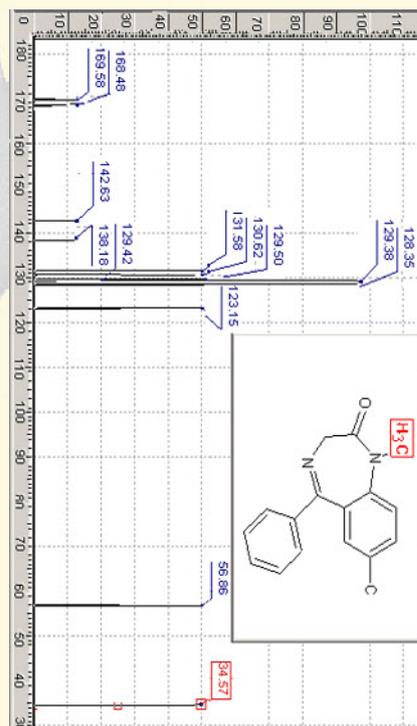
ICSD

DETERM ... on the WEB

Thermophysical Properties of Pure Substances & Mixtures



No.	T boiling K	vapor pres Pa
1	260.74	0.10
2	265.99	0.20
3	269.16	0.30
4	271.45	0.40
5	273.26	0.50
6	274.75	0.60
7	276.03	0.70
8	277.14	0.80
9	278.13	0.90
10	279.03	1.0



Mid-Range Facility Review

News

As part of an overall review process, over 15 mid-range Facilities, supported by the EPSRC, were asked to prepare and submit a Statement of Need (SoN). The intention was that these should come from the communities served by the Facilities rather than the organisations currently providing these services.

An 'iPetition' had been put in place for the benefit of all community members with an interest in the continued availability of the kind of facilities that are currently provided by the CDS. It gave an opportunity for everyone to lend their support and, if they so wish, to contribute to the framing of the SoN. Over 800 people expressed their support for such a facility

Thank you to everyone who signed the iPetition and gave their support in this exercise.

A panel met at the end of July to consider these SoN's and to decide on future funding (if any) of this and the other facilities. The following was received in August:

“The review panel recognised the importance of such a facility and thought it to be a priority for EPSRC support.

The EPSRC cannot guarantee future funding at this stage, but next year the Physical Sciences and Research Infrastructure programmes will be actively reviewing the best way to fund such a facility once the current funding for the database ends in March 2011.

More on the outcome can be found at:

<http://www.epsrc.ac.uk/ResearchFunding/FacilitiesAndServices/outcome.htm>

Login Changes

All users who wish to access the databases via the web must first log in. The home page has been changed so that you can easily login. Most people will also be able to use their Institutional Login.

See the next page about generating a replacement password.

We recommend that you bookmark the CDS homepage <https://cds.dl.ac.uk/> rather than trying to link directly to individual databases (links may change). By accessing systems via the front page you will also see the latest News Items. Alternatively, you can use <https://cds.dl.ac.uk/login> to login prior to access.

Access to all web based database systems is available when you click on the **Access Data** menu option at the top left-hand area on all CDS web pages.

Update Your Registration Details

News

Please check the current address and other registration details we have on file, and if appropriate updates these. If you have changed site and/or we do not have your most up to date email address, phone number or other details you can easily change them.

This link is available via the top pulldown menu on all CDS web pages under the heading "[Registration](#)". If you wish to update your email address, you will need to provide a valid .ac.uk one. If you encounter any difficulties in updating your details then contact us at cdsbb@dl.ac.uk



Generate a Replacement Password

If you have lost your password, you can now generate a replacement one online. All you need to know is your ID. Access is via the "[Registration](#)" pull-down menu on all CDS web pages, under "Lost Password or Unsubscribe".

The New password Request Facility for CDS Users

CDS username

On submission, an automatic email will be sent to the email address that we have on file for you. This contains a web link. This link will allow you to generate a temporary password when accessed by a web browser. This password should be changed to a permanent one via the "[Registration](#)" pull-down menu on the home page, under "[Change your Password](#)" [or directly at <https://cds.dl.ac.uk/pass.html>]

Twitter

News items are now available on twitter. [cds_daresbury](#) has been set up for you to follow and obtain the latest information or you could just select the link from the CDS home page.

Crystallography

New Updates

Cambridge Structural Database System

Version CSD V5.30 (2009 Release)

The latest update (27/05/09) includes 10,821 new entries.
The total number of entries is now 483,021

ICSD Update

The latest ICSD update (2009/1) contains 12,536 more entries as compared to Version 2008/2. The total number of entries is now **120,794**

At present, the ICSD contains:

- 1,400 crystal structures of the elements
- 23,000 records for binary compounds
- 42,500 records for ternary compounds
- 45,000 records for quarternary and quintenary compounds
- About 90,000 entries (70,3%) have been assigned a structure type.

There are currently 4,860 structure prototypes.

By the time you read this, update 2009/2 should have arrived which will take the total number of entries to **123,357**.

Quality Management

The content of ICSD goes through an ongoing re-evaluation and update procedure. Each year around 7,000 new structures are added while the existing content will be modified, complemented or duplicates removed.

Work started in 2008 on the incorporation of legacy crystal structure data on metallic and intermetallic compounds from FIZ Karlsruhe's cooperation partner, The National Institute of Standards & Technology (NIST). This includes testing and duplicate checking besides an extensive evaluation process.

For example, in the 2009/2 update, 29 entries will be removed and 2,794 entries modified. The database will include 1,380 structures from the NIST metals data for which the atomic coordinates have been calculated.

CRYSTMET

The latest release of the CrystMet data (updated 11/06/09) is 4.0.1.

There are 11,411 new entries in this release.

The total number of entries is now **126,413**

New Updates and News

CrystalWeb

CrystalWeb provides a full range of search facilities (author, journal, formula, compound name, atom coordination environment, etc.) on ALL the major crystallographic databases (including CSD) within a single web browser interface.

In addition data from the Southampton Crystallographic Repository is harvested and made available via this interface.

Link with ChemSpider

CrystalWeb hit page now has facility for searching ChemSpider (using InChI codes)



ChemSpider Search (click image)

This is an experimental system to search ChemSpider databases using molecules matched in CrystalWeb. Structure matching currently ignores stereochemistry.

On clicking the image, a page is produced that shows one box for each molecule in the structure, labelled with its molecular formula. Below each formula there is a button to link with ChemSpider.

<chem>3C18H15P.C12H24O6.K.Os.3H</chem> <input type="button" value="Submit"/>	<chem>3C18H15P.C12H24O6.C4H8O.K.Os.3H</chem> <input type="button" value="Submit"/>	<chem>C4H8O</chem> <input type="button" value="Submit"/>
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Click the Submit button to start the ChemSpider search in a new window.

Note: A lot of the molecules will not be in ChemSpider, especially those containing **inorganic** atoms.

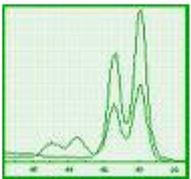
1 hit(s) found in 0.23 seconds
Search term: InChIKey=WYURNTSHIVDZCO-UHFFFAOYAI
Found by InChIKey (full match)

The ChemSpider entry may contain data such as:-

- Names and Synonyms
- Appearance
- Toxicity and Safety Data
- Experimental and Predicted Physchem Properties
- Associated Data Sources and Commercial Suppliers
- and may even show spectra.

SPECTRA

- **Type:** HNMR
- Approved:** No

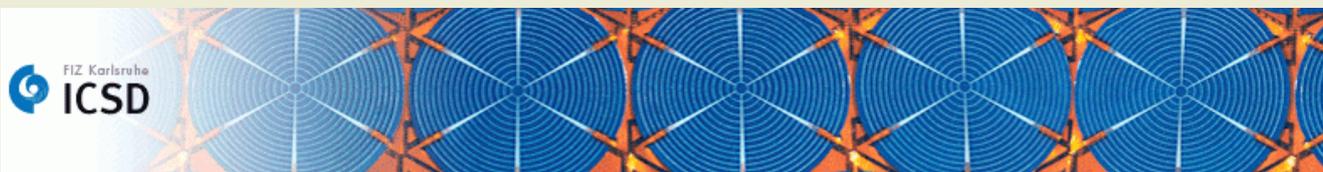


Crystallography

News

Inorganic Crystal Structure Data

A new Web interface to ICSD has been announced by [FIZ Karlsruhe](http://www.fiz-karlsruhe.de) and may soon be available via the CDS.



New Features of ICSD Web

- New and extended information about ICSD including complete Help information
- Enhanced search functionality: easy to use and intuitive search interface
- Easy analysis of large and complex data sets
- Simple and powerful query management: load, modify and save queries

Navigation	Basic Search
Basic search & retrieve	Bibliography
Advanced search & retrieve	Authors <input type="text"/>
Bibliography	Title of Journal <input type="text"/>
Cell	Year of Publication <input type="text"/>
Chemistry	Cell & Symmetry
Symmetry	Cell Parameters <input type="text"/>
Crystal Chemistry	Cell Volume <input type="text"/>
Structure Type	Space Group <input type="text"/>
Experimental Information	Symbol/ Number <input type="text"/>
DB Info	Crystal class <input type="text"/>
Query Management	Chemistry
Load/Modify Queries	Composition <input type="text"/>
Save Queries	ANX Formula <input type="text"/>
Delete Queries	Cryst. Comp. <input type="text"/>
	AB Formula <input type="text"/>
	Chem. Comp. <input type="text"/>
	Exp. Info & Ref. Data
	New Data Only <input type="checkbox"/>
	Collection Code <input type="text"/>
	PDF Number <input type="text"/>
	Release Tag <input type="text"/>
	Volume <input type="text"/>
	Page <input type="text"/>
	Cell Parameters <input type="text"/>
	Cell Volume <input type="text"/>
	Space Group <input type="text"/>
	Symbol/ Number <input type="text"/>
	Crystal class <input type="text"/>
	Crystal System <input type="text"/>
	Pearson Symbol <input type="text"/>
	Number of Elements <input type="text"/>
	Tolerance +/- <input type="text"/> %
	Temperature <input type="text"/>
	Pressure <input type="text"/>

New Navigation menus allow enhanced searching and display of result details

Details
Expand All Collapse All
▶ Visualization
▶ Chemistry
▶ Published Crystal Structure Data
▶ Standardized Crystal Structure Data
▶ Distances & Angles
▶ Bibliography
▶ Experimental Information
▶ Warnings & Comments
▶ Compare Published & Standardized Structure

Organic Chemistry

News

CDS are looking to make the Accelrys and ISIS (now Symyx) databases available again.

Accelrys Databases.

Various Accelrys databases are being "sunsetted" which means that they will not be updated or supported (and so not available) beyond the new year. CDS are looking into the possibility of obtaining a perpetual licence for the following databases:-

* **Protecting Groups** * **Solid Phase Synthesis** * **BioCatalysis**

If successful, we will make them accessible via Accord software, using the Accelrys Database Explorer client software for PC's. We will then look to extend access for everyone via a web interface.

Symyx/Isentris Databases

CDS, in conjunction with JISC, are looking to re-establish the databases that we used to offer in the past using ISIS software, but will now be based on Isentris software.

An evaluation is planned to take place early next year. All databases from Symyx (see below) will be made available over this trial period. Access will be via an Isentris client and possibly via DiscoveryGate.

Databases

Bioactivity

- * Comprehensive Medicinal Chemistry (CMC)
- * MDL Drug Data Report (MDDR)
- * Metabolite
- * National Cancer Institute Databases - The NCI 127K, Plated Compounds, AIDS, and Cancer databases
- * Toxicity - A compendium of toxicological data.
- * RTECS (Registry of Toxic Effects of Chemical Substances)

Sourcing Databases

- * Symyx Available Chemicals Directory (ACD)
- * Symyx Screening Compounds Directory (SCD)

Synthesis Databases

- * ChemInform Reaction Library (CIRX)
- * Current Synthetic Methodology (CSM)
- * Derwent Journal of Synthetic Methods (DJSM)
- * ORGSYN Database
- * Reference Library of Synthetic Methodology (RefLib)
- * Solid-Phase Organic Reactions (SPORE)
- * SPRESI (also available now via CDS)

Funding of the databases has still to be worked out, but it is likely that the following 'packages' would be offered on an Institutional or UK wide model.

'**Discovery Package**' which includes all the Bioactivity, Sourcing and Synthesis Databases
'**Synthesis Package**' - ACD plus Synthesis Databases
'**Pharmacology Package**' - all the Bioactivity databases.

Research Highlight

Dioxygen reduction catalyzed by dicobalt Pacman complexes

Jason B. Love (j.b.love@ed.ac.uk)

This work was funded by the Universities of Nottingham and Edinburgh, The Nuffield Foundation, and the British Mass Spectrometry Society.

The development of fuel cell technologies for automotive use in particular is integral to clean and sustainable energy generation, and relies on catalysts to carry out fundamental chemical redox reactions at the electrodes.^[1] At present, the four-electron reduction of dioxygen to water that occurs at the cathode is the most problematic as it is catalysed by expensive Pt metal that requires considerable overpotentials and has limited long-term stability. As such, there is increasing effort to find cheaper and more durable alternatives which requires a fundamental understanding of the mechanism of this reaction.^[2]

Molecular metal complexes often provide great insight into the detail of a chemical reaction as geometric and electronic structures can be elucidated in solution and the solid state. In particular, dicobalt cofacial or Pacman diporphyrins have proved extremely efficient as catalysts for selective dioxygen reduction, and have allowed many facets of this reaction to be characterised (Fig. 1).^[3] In these complexes, the coordination geometries of the metals and their relative positions are predetermined by the ligand design, and this feature has been shown to be critical to the selectivity of the reduction reaction.

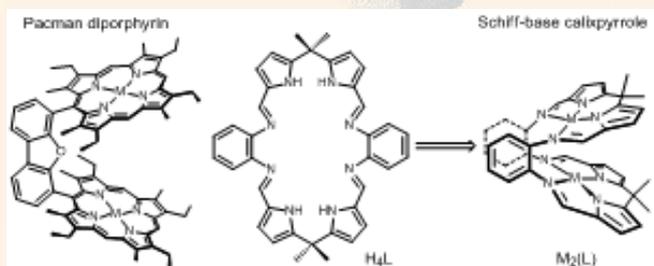


Figure 1 Comparison of Pacman diporphyrin and Schiff-base pyrrole macrocyclic Pacman complexes

As an alternative, we have developed the metallation chemistry of new, straightforwardly-prepared macrocyclic ligand H₄L (Fig. 1) and have found that its metal complexes adopt double-pillared Pacman structural geometries, both in solution and in the solid state; as such, these

complexes are similar to cofacial diporphyrins.^[4] A structural survey of a series of Pd₂(L) complexes in which the ligand periphery was varied showed that this bimetallic microenvironment is less flexible than in the porphyrinic analogues, which would likely have a significant effect on the chemistry of these compounds.^[5]

The chemistry of the dicobalt complexes Co₂(L) has been particularly interesting. The reaction between Co₂(L) and air was found to form a 90:10 mixture of two related complexes, the peroxo complex Co₂(O₂)(L) and the one-electron oxidised superoxo cation Co₂(O₂)(L)⁺.^[6] The solid state structure of the pyridine adduct of the peroxo complex was determined and showed that the O₂ was bound between the two metals in the cleft and adopted a zigzag “Pauling” bonding mode. This was the first time that the structure of any dicobalt Pacman complex containing a reduced form of O₂ had been described. The solid state structure of the acetonitrile adduct of Co₂(O₂)(L) was also determined, and showed a 0.02 Å elongation of the O-O distance (1.389 Å) in the solid state (Fig. 2).^[7] However, DFT calculations indicated that the O-O bond distance was not a good indicator of the degree of formal reduction of O₂ and the apparent similarity in the O-O distance was more likely to be a consequence of the constrained cleft environment.

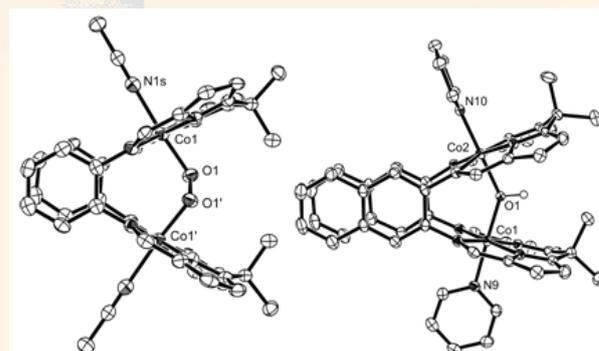


Figure 2 X-ray structures of the peroxo complex Co₂(O₂)(MeCN)₂(L) and the hydroxide

Dioxygen reduction catalyzed by dicobalt Pacman complexes

Continued

The catalytic chemistry of these complexes was studied in acid solution, and showed that while they acted as catalysts for the four-electron reduction of dioxygen to water, the turnover number was low. It was reasoned that this is due to the low concentration of the catalytically active species, the superoxo cation $\text{Co}_2(\text{O}_2)(\text{L})^+$ and the formation of bridged hydroxyl complexes such as $\text{Co}_2(\text{OH})(\text{L})^+$, one of which was characterised structurally (Fig. 2).

At present, we are investigating ligand modifications that inhibit the formation of mono-atom bridged compounds through the use of sterically-hindered *meso*-substituents or elongated aryl hinge groups, and have recently found that $\text{M}_2(\text{L})$ complexes of these new ligands have very different bimetallic cleft environments in the solid state.^[8]

The characterisation of these metal complexes in the solid state by X-ray crystallography allows us to determine key parameters such as $\text{M}\cdots\text{M}$ separation, M-L and O-O bond distances, and the overall shape of the complex (*i.e.* Pacman or not?). This information is invaluable to us in constructing structure-activity relationships and to assist in the design new ligands that build on these features. Access to the Cambridge Crystallographic Database is important as it allows us to compare structural data accurately and efficiently in ConQuest, in particular using defined bond distances or short contacts such as hydrogen bonding interactions, to manipulate known chemical structures using tools such as Mercury, and to analyse large series of bond distances in Vista to determine ranges and means for selected bonds *e.g.* peroxo O_2^{2-} versus superoxo O_2^- .

- [1] R. Bashyam, P. Zelenay, *Nature* **2006**, *443*, 63; M. Lefèvre, E. Proietti, F. Jaouen, J.-P. Dodelet, *Science* **2009**, *324*, 71.
- [2] B. Wang, *J. Power Sources* **2005**, *152*, 1; J.-M. Savéant, *Chem. Rev.* **2008**, *108*, 2348.
- [3] J. P. Collman, P. S. Wagenknecht, J. E. Hutchinson, *Angew. Chem. Int. Ed.* **1994**, *33*, 1537; J. Rosenthal, D. G. Nocera, *Acc. Chem. Res* **2007**, *40*, 543.
- [4] J. B. Love, *Chem. Commun.* **2009**, 3154
- [5] G. Givaja, M. Volpe, J. W. Leeland, M. A. Edwards, T. K. Young, S. B. Darby, S. D. Reid, A. J. Blake, C. Wilson, J. Wolowska, E. J. L. McInnes, M. Schröder, J. B. Love, *Chem. Eur. J.* **2007**, *13*, 3707.
- [6] G. Givaja, M. Volpe, M. A. Edwards, A. J. Blake, C. Wilson, M. Schröder, J. B. Love, *Angew. Chem. Int. Ed.* **2007**, *46*, 584.
- [7] M. Volpe, H. Hartnett, J. W. Leeland, K. Wills, M. Ogunshun, B. Duncombe, C. Wilson, A. J. Blake, J. McMaster, J. B. Love, *Inorg. Chem.* **2009**, *48*, 5195.
- [8] E. Askarizadeh, A. M. J. Devoille, D. M. Boghaei, A. M. Z. Slawin, J. B. Love, *Inorg. Chem.* **2009**, *48*, 7491.

Databases Available From The Chemical Database Service

A brief description of all the databases currently available from the CDS at Daresbury.

STRUCTURES

The Structures databases contain a comprehensive collection of organic, organometallic and inorganic compounds, metals, and alloys **crystal structure data**.

CSD - Cambridge Structural Database.

Crystal structure data for over **494,000 organic and organo-metallic compounds**. New releases of this database are received and mounted quarterly.

- * **ConQuest** is the graphical front end which has 3D search capabilities.
- * **VISTA** performs numerical, statistical and graphical analyses.
- * **Mercury** provides comprehensive facilities for visualising crystal structures in three dimensions.
- * **IsoStar** A knowledge base of non-bonded interactions derived from the CSD, the Protein Data Bank (PDB) and molecular orbital calculations. Uses a simple web interface.
- * **Mogul** A knowledge base of molecular geometries using data derived from the CSD.

ICSD - Inorganic Crystal Structure Data File.

Crystal structure data for over **120,700 inorganic compounds**

WWW interface available.

CRYSTMET

Crystal structure data for over **126,400 metals, alloys and intermetallics**.

CDIF - Crystal Data Identification File.

Crystal class and unit cell data for **237,671 crystal Structures**.

CrystalWeb

A simple **web interface to all of the crystallographic databases** that allows bibliographic and cell data searching along with structure display.

UTILITY PROGRAMS

A variety of utility programs are available, including links to electronic literature, chemical file format conversion and molecule viewers.

SPECTROSCOPY

The Spectroscopy databases are designed to aid the chemist in structure elucidation and spectra interpretation problems.

SPECINFO

SpecInfo is a multi-technique spectroscopic database system which covers NMR, IR and mass spectra. A variety of features are available within the program to help with spectrum prediction and searching. It is accessed via the Web interface **SpecSurf**.

ACD/Labs I-Lab

The data can be accessed via **ChemSketch**, a PC based structure drawing package or via the Web using the graphical interface **I-Lab**. In addition to NMR searching and prediction, ACD/Labs I-Lab has compound name generation and property prediction programs.

The databases currently contain:-

No.of Records	13C NMR	1H NMR	15N NMR	17O NMR	31P NMR	19F NMR	11B NMR
SPECINFO	359,647	130,025	7,661	5,184	16,561	25,442	10,238
ACD/Labs	200,100	210,700	9,287	-	27,500	17,000	-

SPECINFO IR Spectra = 20,898 Mass Spectra = 138,727

ACD/Labs Physicochemical data:

pKa = 16,000 LogP = 18,400 Solubility = 5,000

Physical property predictions includes pKa, LogP, LogD, aqueous solubility, boiling point/vapour pressure/enthalpy of vaporization, adsorption coefficient/bioconcentration.

PHYSICAL CHEMISTRY

DETERM

One of the world's largest thermophysical property databases of pure compounds and compound mixtures. Contains nearly **6 Million data sets** for around **134,000 systems** (around 28,000 pure substances and 106,000 mixtures) covering around **500 property fields**.

Detherm can be accessed via Client server software or via a Web interface.

ORGANIC CHEMISTRY

SPRESI

Allows you to search Molecules, Reactions, References and associated data. Contains synthesis planning tool.

Direct access over the web to:-

- 7.0 million structures
- 3.9 million reactions
- 31.7 million factual data entries

extracted from:- 645,000 references
164,000 Patents

Available Chemicals

Up-to-date catalogue data including prices for:-

- * Sigma-Aldrich
- * Acros/Maybridge
- * FluoroChem
- * Apollo.

using ChemAxon's JChem software over the web.

Screening Compounds

Libraries from 11 Suppliers are available for searching using ChemAxon's JChem software over the web.

General Information

The Chemical Database Service provides on-line access to a variety of quality databases in the field of Chemistry, plus support, training and advice to the UK academic community.

The Service is available **free of charge at point of access** to UK academic research groups for non-commercial work. Each individual user will be issued with a unique ID. **It is not our policy to allow shared ID's.**

Main Service Machine

cds.dl.ac.uk

CDS Helpdesk:
cdsbb@dl.ac.uk
or phone
01925 603 162

Web Site

Information about CDS, including online help, documentation and up-to-date news items is available over the World Wide Web at the CDS website.

<https://cds.dl.ac.uk>

Web based interfaces to selected Databases are also available from this site.

Comments:

All comments, questions and suggestions about this newsletter should be sent to:

Dr. D. Parkin

Email: donald.parkin@stfc.ac.uk

Phone: 01925 603 162

Links used in this Newsletter can be found at:

<http://cds.dl.ac.uk/letterlinks>

Documentation:

Most documentation is available online or within the client packages. User Guides, training exercises and tutorials can all be downloaded from the CDS web site.

CHEMICAL DATABASE SERVICE

Daresbury Laboratory

Warrington

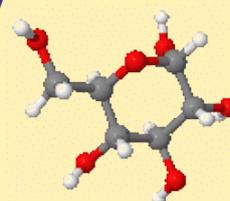
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CDS
ON-LINE